699. *Mechanism of the Azide–Nitrite Reaction. Part III.*[1] *Reaction in* [^{18}O]*Water.*

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The isotopic composition of the nitrous oxide evolved when nitrous acid and hydrazoic acid react in [^{18}O] water has been studied under conditions in which the kinetics and mechanism of the chemical reaction are known. The variation of the enrichment of the evolved nitrous oxide after complete reaction, with the concentration of azide, and with the acidity, shows that there is no appreciable hydrolysis of the intermediate nitrosyl azide in aqueous solution; all of it breaks down to nitrogen and nitrous oxide. The results show that there is exchange of oxygen atoms between nitrous acid and water with a rate law $v = k[H^+][HNO_2]$, where $k = 230$ sec.$^{-1}$ mole^{-1} l. at 0°. This has been confirmed by direct measurements of the rate of exchange of oxygen atoms between nitrous acid and water at 0°, oxygen-18 being used as a tracer. The results offer a partial explanation of discrepancies between the results of several previous investigations of oxygen exchange between nitrous acid and water, and of the kinetics of various reactions of nitrous acid, and suggest an exchange mechanism with direct attack of water upon the nitrous acidium ion, $H_2NO_2^+$, when the concentration of nitrite ion is low ($<0{\cdot}05$N). At higher concentrations of nitrite ion, exchange is by formation of dinitrogen trioxide.

WHEN initially isotopically normal nitrous acid reacts with hydrazoic acid in [^{18}O]water, the evolved nitrous oxide is enriched in oxygen-18:

$$HNO_2 + HN_3 \longrightarrow N_2O + N_2 + H_2O$$

Under suitable conditions the amount of exchange between nitrous acid and the solvent during the chemical reaction can be kept relatively small (<10% of the value for complete isotopic equilibration). If the reaction is always carried out under a given set of conditions, and suitable control experiments are run, reliable and consistent results can be obtained, and it is possible to use this reaction as a method of analysing for the oxygen-18 content of nitrous acid.[2] Our present object was to carry out the azide–nitrite reaction in [^{18}O] water, and to obtain information about the rate and mechanism of the exchange of oxygen atoms between nitrous acid and water from the observed enrichment of the evolved nitrous oxide. The method used was to allow " nitrite " to react with a large excess of azide under conditions where previous work [1] had revealed the rate equation and mechanism of the chemical reaction. By " nitrite " we mean all of the species present in solution that are collectively analysable as nitrous acid. In the present work the concentrations of " nitrite " were low, $<0{\cdot}05$M, and the acidity was also low, $[H^+] < 0{\cdot}2$M. Under these conditions molecular nitrous acid, HNO_2 and the nitrite ion, NO_2^- were the only species present in appreciable concentration. Hence

$$[\text{" nitrite "}] = [HNO_2] + [NO_2^-]$$

Either the " nitrite " or the solvent water was initially labelled with oxygen-18. When reaction was complete, the nitrous oxide formed was collected, purified, and analysed mass-spectrometrically.

There have been two previous quantitative investigations of the kinetics of oxygen exchange between nitrous acid and water. Bunton, Llewellyn, and Stedman [3] studied the exchange in the concentration range $[NO_2^-] = 0{\cdot}5$—$2{\cdot}0$M at 0°. They found the rate

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[1] (*a*) Part I, *J.*, 1959, 2943. Part II, *J.*, 1959, 2949.

[2] Anbar and Taube, *J. Amer. Chem. Soc.*, 1954, **76**, 6243.

[3] Bunton, Llewellyn, and Stedman, *Chem. Soc. Special Publ.*, 1957, No. 10, 1957, p. 113; *J.*, 1959, 568.

law to be $v = k_2[HNO_2]^2$, with $k_2 = 0{\cdot}53$ sec.$^{-1}$ mole^{-1} l. They interpreted this result as showing that oxygen exchange was by the formation and rehydration of dinitrogen trioxide:

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \qquad (1)$$

Anbar and Taube [2] studied the exchange between nitrite and water in the presence of phosphate buffers, and concluded that the rate equation was $v = k[H^+][HNO_2]$. They interpreted this as a rate-determining formation and rehydration of the nitrosonium (nitrosyl) ion:

$$H_2NO_2^+ \rightleftharpoons NO^+ + H_2O \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \qquad (2)$$

It was hoped that the present study would throw some light on the cause of this difference in rate equations.

Experimental Method.—To obtain information on the oxygen exchange between water and nitrous acid from the isotopic abundance of the evolved nitrous oxide we must consider the kinetic forms of both exchange and chemical reaction.

Our present experiments were done with reagent concentrations such that the kinetic law was: $v = k'_c$[" nitrite "] (k'_c is constant for a given run, but depends upon $[H^+]$ and [azide]). It can be shown (Appendix) that if oxygen exchange has the rate law, $v = k'_E$ [" nitrite "] (k'_E constant for a given run, but dependent upon $[H^+]$), then with tracer in the solvent water

$$N^*_{N_2O}/(N_{H_2O} - N^*_{N_2O}) = \tfrac{1}{2}k'_E/k'_c$$

($N^*_{N_2O}$ is the isotopic abundance of evolved N_2O at complete reaction, N_{H_2O} is abundance of the water.)

Reaction and Exchange in Azide Buffer.—A series of reactions were carried out, with initially isotopically normal nitrite, and [^{18}O] water as solvent. There was always a large excess of azide buffer over " nitrite," and a large excess of isotopically enriched solvent water. The results are in Table 1.

TABLE 1. *Azide–nitrite reaction in* [^{18}O] *water at* 0°.

No.	$[HN_3]$ (M)	$[N_3^-]$ (M)	$10^5[H^+]$ (M)	[" nitrite "]$_0$ (mM)	$\dfrac{N^*_{N_2O}}{N_{H_2O} - N^*_{N_2O}}$	$\dfrac{10^2[N_3^-]N^*_{N_2O}}{(N_{H_2O} - N^*_{N_2O})}$ (M)	$\dfrac{N^*_{N_2O}}{N_{H_2O}}$
17	0·236	0·279	8·45	25·0	0·158	4·4	0·136
18	0·121	0·190	6·35	19·7	0·226	4·3	0·183
19	0·060	0·251	2·40	19·7	0·163	4·1	0·139
26	0·294	0·0377	78·0	4·4	1·38	5·2	0·665
27	0·113	0·219	5·15	11·4	0·270	5·9	0·223
28	0·191	0·360	5·30	3·5	0·131	4·7	0·115
29	0·219	0·352	6·20	3·8	0·139	4·9	0·121
30	0·225	0·344	6·55	17·9	0·177	6·1	0·152
31	0·225	0·344	6·55	17·8	0·189	6·5	0·162
32	0·181	0·371	4·9	6·6	0·148	5·5	0·129
35	0·046	0·0703	6·55	6·7	0·727	5·1	0·422
36	0·044	0·067	6·60	8·4	1·044	7·0	0·521
43	0·119	0·184	6·45	3·4	0·386	7·1	0·276
44 [a]	0·022	0·046	4·55	2·6	1·170	5·4	0·540
45 [b]	0·022	0·046	4·55	2·6	0·370	1·7	0·268
46 [c]	0·022	0·046	4·55	2·6	0·390	1·8	0·280

[a] 0·406M-$NaClO_4$ added. [b] 0·406M-NaBr added. [c] 0·406M-NaCl added.

The ratio $N^*_{N_2O}/(N_{H_2O} - N^*_{N_2O})$ is sensibly independent of the concentrations of both nitrite and hydrogen ions, but it is dependent upon the concentration of azide ions (Figure). If exchange had the kinetic form $v \propto$ [" nitrite "]^n, $n \neq 1$, then $N^*_{N_2O}/(N_{H_2O} - N^*_{N_2O})$ would vary with the concentration of nitrite. Thus we establish that in the conditions of these experiments there is an oxygen exchange which is of the first order with respect to the concentration of " nitrite."

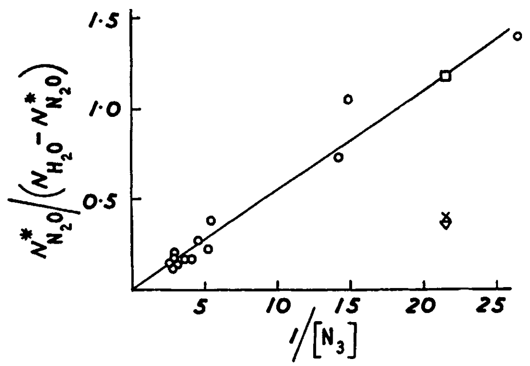
The kinetics of the azide–nitrite reaction in the presence of a large excess of azide buffer have been described in Part II. The rate equation is $v = k_3^{N_3^-}[H^+][HNO_2][N_3^-]$. There are two reasonable mechanisms for this reaction which are consistent with this rate equation. One is the formation of nitrosyl azide by a rate-determining attack of azide ions on an equilibrium concentration of nitrosonium ions, followed by a rapid breakdown of nitrosyl azide to the final products:

$$H_2NO_2^+ \underset{\text{fast}}{\rightleftharpoons} NO^+ + H_2O \xrightarrow[\text{slow}]{N_3^-} N_3NO \xrightarrow[\text{fast}]{} N_2 + N_2O$$

The other possibility is a rate-determining nucleophilic attack by the azide on the nitrous acidium ion to form nitrosyl azide, which breaks down in a subsequent fast step:

$$H_2NO_2^+ + N_3^- \xrightarrow[\text{slow}]{} H_2O + N_3NO \xrightarrow[\text{fast}]{} N_2 + N_2O$$

The first of these mechanisms would require the rate of oxygen exchange between nitrous acid and water by the formation and rehydration of the nitrosonium ion to be much more rapid than the rate of the chemical reaction to form nitrous oxide, and hence it would be expected that the evolved nitrous oxide would have the same isotopic composition as the solvent. The results in the final column of Table 1 show that the enrichment of the nitrous oxide in oxygen-18 is much less than that of the solvent water, and hence that mechanism (2) must be rejected.



Relation between concentration of azide and the isotopic abundance of the nitrous oxide evolved.
□ $NaClO_4$, 0·406M. ∇ NaBr, 0·406M. × NaCl, 0·406M.

Previous work[1,3,4] has shown that the rate equations for the formation of the nitrosyl compounds NOX, where X = Cl, Br, NCS, I, NO_2, and N_3 are of the form $v = k_3^{X^-}[H^+][HNO_3][X^-]$, and that the values of $k_3^{X^-}$ vary by less than a factor of three. We therefore conclude that mechanisms analogous to (2) must be rejected in all these cases; a similar conclusion has been drawn for diazotisation.[4]

The results in the seventh column of Table 1 and in the Figure show that the quantity $[N_3^-]N^*_{N_2O}/(N_{H_2O} - N^*_{N_2O})$ is approximately constant over a wide range of values of $[HN_3]$, $[N_3^-]$, $[H^+]$, and $[\text{“ nitrite ”}]_0$, except in the presence of added halide ion. As the rate equation for chemical reaction is $v = k_3^{N_3^-}[H^+][HNO_2][N_3^-]$ the rate equation for oxygen exchange must be $v = k[H^+][HNO_2]$. The value of $k_3^{N_3^-}$ is 2340 sec.$^{-1}$ mole^{-2} l.^{2}; from the results in Table 1, it follows that $k \simeq 260$ sec.$^{-1}$ mole^{-1} l. This value is subject to a considerable uncertainty (*ca.* ±20%).

The above results also show that there is no significant exchange by the hydrolysis of

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[4] Hughes, Ingold, and Ridd, *J.*, 1958, 58, and accompanying papers.

nitrosyl azide. If we suppose that a fraction, α, of all of the nitrosyl azide molecules formed are hydrolysed back to nitrous and hydrazoic acids:

$$N_3NO + H_2{}^{18}O \longrightarrow H_2N^{18}OO^+ + N_3^- \xrightarrow[\text{fast}]{} HN^{18}OO + NH_3$$

while the remaining fraction, $1 - \alpha$, breaks down to nitrogen and nitrous oxide:

$$N_3NO \longrightarrow N_2 + N_2O$$

then it is clear that (rate of exchange)/(rate of reaction) $= k'_E/k'_c = 2N^*_{N_2O}/(N_{H_2O} - N^*_{N_2O}) = \alpha/(1 - \alpha)$, and should be independent of the azide concentration, and there would be a positive intercept at $1/[N_3^-] = 0$ in the Figure. The results show that k'_E/k'_c is proportional to $[N_3^-]^{-1}$. There is no sign of any component in the rate equation for exchange leading to a value of k'_E/k'_c independent of $[N_3^-]$, and hence there is no appreciable hydrolysis of nitrosyl azide.

Reaction in Excess of Perchloric Acid.—The above results refer to oxygen exchange at relatively low acidities (pH $\sim$ 5). At higher acidities ($[H^+] > 0{\cdot}05$M) and with suitable concentrations of nitrous and hydrazoic acids, the azide–nitrite reaction has the mechanism:

$$HN_3 + H_2NO_2^+ \xrightarrow[\text{slow}]{} H^+ + H_2O + N_3NO \xrightarrow[\text{fast}]{} N_2 + N_2O$$

The rate equation is $v = k_3^{HN_3}[H^+][HNO_2][HN_3]$. By carrying out isotopic experiments similar to those described in the previous section it is possible to make quantitative measurements of the rate of oxygen exchange between nitrous acid and water at acidities where exchange would be too fast for direct measurement. All previous measurements of oxygen exchange between nitrous acid and water have been made at low acidities (pH > 4·5).[2,3]

A slight modification of the procedure is necessary. For reaction in azide buffers, with concentration of azide ions >0·05M, the rate of the chemical reaction is markedly greater than the rate of oxygen exchange, and hence the difference between $N^*_{N_2O}$ and N_{H_2O} is large enough for accurate measurement. For reaction in excess of perchloric acid the rate of chemical reaction is much less than the rate of exchange. This is because in azide buffers the species attacking the nitrous acidium ion is the azide ion, while in excess of perchloric acid it is the much more weakly nucleophilic hydrazoic acid. As the chemical rate is much less than the exchange rate, the value of $N^*_{N_2O}$ is only slightly less than N_{H_2O}. Hence $N_{H_2O} - N^*_{N_2O}$ cannot be accurately measured. To overcome this difficulty, reaction was carried out with initially isotopically enriched sodium nitrite, in isotopically normal water (then the evolved nitrous oxide is only slightly enriched in oxygen-18). The equation relating the isotopic abundance of reactants and products can be rearranged to:

$$(N_{Nit} - N^*_{N_2O})/N^*_{N_2O} = \tfrac{1}{2}k'_E/k'_c$$

where N_{Nit} = atoms % excess of oxygen-18 in the nitrite, initially. The quantities $N^*_{N_2O}$ and $N_{Nit} - N^*_{N_2O}$ can be measured accurately (Table 2). The rate equation for chemical reaction under these conditions is $v = k_3^{HN_3}[H^+][HNO_2][HN_3]$. The sixth row of Table 2 shows that the quantity $[HN_3](N_{Nit} - N^*_{N_2O})/N^*_{N_2O}$ is approximately constant.

TABLE 2. *Isotopic experiments on the azide–nitrite reaction in excess of perchloric acid at 0°.*

No.	47	51	49	48	50
$[H^+]$ (M)	0·017	0·107	0·048	0·278	0·278
$[HN_3]$ (M)	0·175	0·035	0·175	0·175	0·175
$10^2[HNO_2]$ (M)	0·41	0·41	0·41	0·41	4·0
$10^2(N^*_{N_2O}/N_{Nit})$	4·56	1·06	4·52	5·2	5·86
$[HN_3]$ $(N_{Nit} - N^*_{N_2O})/N^*_{N_2O}$ (M)	3·7	3·3	3·7	3·5	2·8

The rate equation for exchange is therefore $v = k[H^+][HNO_2]$. If $k_3^{HN_3}$ is taken to be 34 sec.$^{-1}$ mole^{-2} l.^{2}, $k = 230$ sec.$^{-1}$ mole^{-1} l. at 0°.[2] This value is again subject to considerable uncertainty (*ca.* ±20%), but is in good agreement with the value of 260 sec.$^{-1}$ mole^{-1} l. obtained from the experiments in azide buffers. As the two sets of measurements were made in quite different regions of acidity, ($[H^+] = 0{\cdot}02$—$0{\cdot}28$M, and $[H^+] = 0{\cdot}24 \times 10^{-5}$—$7{\cdot}8 \times 10^{-5}$M) and with different mechanisms and rate equations for the azide–nitrite reaction, this " competition " method appears to be quite reliable for the determination of the rate of exchange. We consider that it should be generally applicable, and it may be of value in systems in which the rate of one of these processes is too fast for convenient measurement but the rate of the other can be determined, possibly indirectly.

The kinetic forms of the oxygen exchange do not of themselves prove that the nitrous acidium ion is formed in a pre-equilibrium proton transfer, and formulations in terms of a general acid catalysis by the proton or by molecular nitrous acid would be kinetically indistinguishable. However it is extremely difficult to formulate common mechanisms for nitrosations by nitrous acid, except by assuming that they all have the common feature of nucleophilic attack upon a preformed nitrous acidium ion (cf. refs. 1, 2, 3, 4).

We estimate $k_3^{H_2O}$, the third-order rate constant for bimolecular attack of an individual water molecule upon the nitrous acidium ion, to be 4 sec.$^{-1}$ mole^{-2} l.^{2} at 0°, *i.e.*, 1/8th that of hydrazoic acid, and *ca.* 1/150th that of the azide ion.

We can now consider the results of experiments 44, 45, and 46 (Table 1). These show that chloride and bromide ions decrease the enrichment of the evolved nitrous oxide, although perchlorate ions (in this low concentration) have no effect. Halide ions introduce a new reaction path for both exchange and chemical reaction, because nitrosyl halide (X = Br or Cl) can be formed and react with either water or azide.

$$X^- + H_2{}^{18}O{\cdot}NO^+ \xleftarrow{H_2{}^{18}O} NOX \xrightarrow{N_3^-} N_3NO + X^- \longrightarrow N_2 + N_2O$$

It appears from diazotisation experiments that nitrosyl halides are less reactive electrophiles than the nitrous acidium ion.[4] Thus they will discriminate between the abundant, but unreactive, water molecules, and the less abundant, but much more reactive, azide ions in favour of the latter, relative to the behaviour of the nitrous acidium ion. Hence the isotope abundance of the evolved nitrous oxide will be decreased by addition of halide ions.

Mechanism of Oxygen Exchange between Nitrous Acid and Water at 0°.—Previous studies [3] showed that in much more concentrated solutions of sodium nitrite (0·5—2·0M) and with concentrations of nitrous acid from 0·01 to 0·1M, the rate equation for exchange was $v \propto [HNO_2]^2$ and not $\propto [H^+][HNO_2]$. Anbar and Taube [2] concluded that there is a mechanism for oxygen exchange between nitrous acid and water with a rate equation $v \propto [H^+][HNO_2]$. However, many of their experiments were complicated by a catalysis of exchange due to the phosphate buffer that they used to control the pH, and their rate constants varied with both buffer composition and concentration. The work described in the previous sections confirms the existence of a mechanism for the exchange of oxygen atoms between nitrous acid and water, with a rate equation of the form $v \propto [H^+][HNO_2]$, and additional evidence for this exchange mechanism, also in the absence of nucleophilic buffers, has been obtained. Three experiments were carried out at 0°, with solutions of [^{18}O] sodium nitrite in isotopically normal water, acidified with perchloric acid. Exchange was stopped at suitable times by adding excess of sodium hydroxide solution. The oxygen-18 content of the nitrite was determined by allowing it to react in a sodium azide–hydrazoic acid buffer, and measuring the oxygen-18 content of the evolved nitrous oxide mass-spectrometrically. Corrections were made for the exchange occurring during reaction with the azide. These were made by using the results given in Table 1, as an empirical correction. The results are given in Table 3. The rates were obtained from two points only, and hence are subject to a considerable uncertainty. (This applies merely to the numerical values of the measured rate. The rate equation for isotopic exchange in a system in chemical equilibrium always has a first-order form with respect to the isotopic abundances and hence no ambiguity arises in calculating the exchange rate.)

TABLE 3. *Oxygen exchange between nitrous acid and water at 0°.*

$10^3[HNO_2]$ (M)	$10^3[NO_2^-]$ (M)	$10^5 v$ (sec.$^{-1}$ mole l.$^{-1}$)	$v/[HNO_2]^2$ (sec.$^{-1}$ mole^{-1} l.)	$v/([HNO_2][H^+]$ (sec.$^{-1}$ mole^{-1} l.)
1·46	9·3	2·0	9·4	230
1·46	18·6	9·6	4·5	240
0·73	9·3	3·6	6·8	180

v is the rate of oxygen exchange between nitrous acid and water, irrespective of tracer. $[H^+]$ is calculated by taking the dissociation constant of nitrous acid [5] as $K = 3{\cdot}2 \times 10^{-4}$ mole l.$^{-1}$.

The values of $v/[HNO_2]^2$ in Table 3 are much greater than the values of k_2, the rate constant for the formation of dinitrogen trioxide. From diazotisation this is 0·85 sec.$^{-1}$ mole^{-1} l.; from oxygen exchange (with concentrations of nitrite ion $>$0·5M) it is 0·53 sec.$^{-1}$ mole^{-1} l. Therefore in the present experiments there is another mechanism leading to exchange between nitrous acid and water, and under these particular conditions it is much faster than the rate of formation and rehydration of dinitrogen trioxide. The results in Table 3 are consistent with a rate equation $v = k[H^+][HNO_2]$, with $k \simeq 220$ sec.$^{-1}$ mole^{-1} l., in agreement with the kinetic form of rate equation and the values of k found by the competition experiments with azide ($k \simeq 260$ sec.$^{-1}$ mole^{-1} l. in azide buffers and $k \simeq 230$ sec.$^{-1}$ mole^{-1} l. in excess of perchloric acid). This provides a direct confirmation that the interpretation of the exchange results from the azide–nitrite reaction is correct, and shows that exchange does not depend in any way upon azide.

There are two possible interpretations of the rate law $v = 230[H^+][HNO_2]$ sec.$^{-1}$ mole l.$^{-1}$ at 0°. One is that exchange occurs by the formation and rehydration of the nitrosonium ion (2). The other possibility is a bimolecular attack by the water molecule on the nitrous acidium ion:

$$H_2NO_2^+ + H_2{}^{18}O \longleftarrow H_2N^{18}OO + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The present results do not distinguish with certainty between these possibilities. The fact that amines and nucleophilic anions can be shown to substitute at the nitrous acidium ion and not at the nitrosonium ion,[1b,4] suggests that mechanism (3) is more likely than (2). Anbar and Taube [2] prefer to interpret their rate equation for oxygen exchange of $v \propto [H^+][HNO_2]$ as a rate-determining formation of the nitrosonium ion (2). They base this interpretation on a comparison of the rates of oxygen exchange and of reaction between nitrous acid and hydrogen peroxide in phosphate buffer, and on the rate of oxygen exchange between nitrous acid and water in the presence of hydrogen peroxide and phosphate buffer:

$$HNO_2 + H_2O_2 \longrightarrow HNO_3 + H_2O$$

In the presence of phosphate buffer they found that with high (4—8M) concentrations of hydrogen peroxide, the rate of the chemical reaction was independent of $[H_2O_2]$, and was of first order in $[H^+]$ and $[HNO_2]$. This rate was similar to the rate of oxygen exchange between nitrous acid and water in the absence of hydrogen peroxide. In the presence of 4M-hydrogen peroxide the rate of exchange between nitrous acid and water was much less than the value in its absence. This led them to suggest that in their experiments nitrosonium ions were captured by hydrogen peroxide as fast as they were formed:

$$H_2NO_2^+ \xrightarrow[\text{slow}]{} NO^+ + H_2O \xrightarrow[\text{fast}]{H_2O_2} HNO_3 + H_2O$$

It is difficult to interpret our experiments in the presence and in the absence of azide as reactions of the nitrosonium ion. If we assume that exchange occurs *via* NO^+ (2) then the kinetic law for the reaction in azide buffers requires that the azide ion reacts with an equilibrium concentration of nitrosonium ions, and we know this to be incorrect.

Thus we would have to assume that the azide ion reacts with predominantly the nitrous

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[5] Klemenc and Hayek, *Monatsh.*, 1929, **54**, 407.

acidium ion, whereas the water reacts with NO^+ but not $H_2NO_2^+$, and it is difficult to reconcile the latter assumption with Anbar and Taube's assumption that hydrogen peroxide captured the nitrosonium ion as fast as it was formed.

This argument says that the nitrosonium ion is specifically reactive towards water, relative to such nucleophiles as amines, hydrazoic acid, or azide and halide ions. This is not true for such reactive cations as the carbonium [6] and chloronium [7] ions. It is difficult to interpret Anbar and Taube's experiments on the reaction between hydrogen peroxide and nitrous acid, but the very high concentrations of hydrogen peroxide (*ca.* 25% w/w) may have had some solvent effect upon the equilibria and rates of both oxygen exchange and the chemical reaction.

The present results show why we obtained a different kinetic law [3] for oxygen exchange between nitrous acid and water from that of others.[2] With no nucleophiles present, other than water and nitrite ions, exchange can occur by reaction (1) and (2) or (3), with rate laws $v = k_3^{NO_2^-}[H^+][NO_2^-][HNO_2] = k_2[HNO_2]^2$, and $v = k[H^+][HNO_2]$ respectively. In our earlier work the concentration of "nitrite" was such that the rate of formation and hydration of dinitrogen trioxide (1) was much greater than any other rate of exchange. From our present results we calculate that exchange by reactions of the nitrous acidium ion would be $<10\%$ of total exchange for M-NO_2^-, and $<20\%$ for 0·5M-NO_2^-.

Anbar and Taube [2] used lower concentrations of nitrite, and here the rates of the two exchange paths are similar. There was also an additional route for exchange, the formation and hydrolysis of a nitrosyl phosphate. This might explain why their rate constants varied with pH and buffer concentration, and why addition of 0·2M-sodium bromide did not affect the exchange rate; there was not enough of it to compete with the other reagents, *i.e.*, water and phosphate ions.

Oxygen exchange between nitric acid and water, catalysed by nitrous acid, has been studied.[8] The rate of xchanege depended on the concentration of "nitrous acid" (by which was meant all of the species present in solution, which on dilution with water can be analysed as nitrous acid) to the first power in 4M-nitric acid, to the second power in 10M-nitric acid, and to the first power in 13M-nitric acid. The rate for a given "nitrous acid" concentration increased with increasing nitric acid concentration. The present results show that the rate of oxygen exchange between "nitrous acid" and water would always be much greater than the observed rate of exchange between nitric acid and water, *i.e.*, the oxygen of the "nitrous acid" was in isotopic equilibrium with the water. This exchange of oxygen atoms between nitrous acid and water cannot be the slow step for the overall exchange. This is of value in eliminating some of the possible mechanisms that could explain results.

APPENDIX

A relation between the rate of exchange between nitrous acid and water, the rate of the azide–nitrite reaction, and the oxygen-18 content of the nitrous oxide evolved for complete reaction, $N^*_{N_2O}$, when one component is labelled with oxygen-18, can readily be derived as follows.

Reaction conditions are chosen such that the rate equation for chemical reaction contains only a first-order term in nitrite, and such that the acidity and azide concentration remain constant during reaction. This requires a large excess of azide over nitrite, and buffering of the solution with excess of perchloric acid or an azide buffer. The rate equation is therefore:

$$d[NO_2^-]/dt = -d[\text{nitrite}]_4/dt = k'_c[\text{nitrite}]$$

(k'_c is a function of acidity and azide concentration). Integration in the conventional manner gives

$$[\text{nitrite}] = [\text{nitrite}]_0 \exp(-k'_c t)$$

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[6] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.

[7] de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

[8] Bunton, Llewellyn, and Halevi, *J.*, 1953, 2653.

If the rate equation for oxygen exchange between nitrous acid and water is also of first order in nitrite, and the tracer is initially in the solvent water

$$v = k'_{\mathrm{E}}[\text{nitrite}] = \frac{2[\text{nitrite}][\mathrm{H_2O}]}{2[\text{nitrite}] + [\mathrm{H_2O}]} \cdot \frac{\mathrm{d}\log_{\mathrm{e}}(N_{\mathrm{H_2O}} - N_{\mathrm{Nit}})}{\mathrm{d}t}$$

N_{Nit} = atom % excess of oxygen-18 in the nitrite. This can be rearranged to $N_{\mathrm{Nit}} = N_{\mathrm{H_2O}}[1 - \exp(\frac{1}{2}k'_{\mathrm{E}}t)]$.

The final concentration of nitrous oxide, $[\mathrm{N_2O}]_\infty$, is equal to the initial concentration of nitrite, $[\text{nitrite}]_0$. We suppose that the isotopic abundance of the nitrous oxide evolved at any instant is that of the nitrite at that instant, *i.e.*,

$$[\mathrm{N_2O}]_\infty N^*_{\mathrm{N_2O}} = \int_0^\infty (\mathrm{d}[\mathrm{N_2O}]/\mathrm{d}t) N_{\mathrm{Nit}} \, . \, \mathrm{d}t$$

by substitution we obtain

$$[\mathrm{N_2O}]_\infty N^*_{\mathrm{N_2O}} = \int_0^\infty N_{\mathrm{H_2O}}(\mathrm{d}[\mathrm{N_2O}]/\mathrm{d}t) \, . \, \mathrm{d}t + \int_0^\infty k'_{\mathrm{c}}[\text{nitrite}]_0 N_{\mathrm{H_2O}} \exp[-(k'_{\mathrm{c}} + \tfrac{1}{2}k'_{\mathrm{E}})t] \, . \, \mathrm{d}t$$

These integrals can readily be evaluated by standard procedures, and rearrangement of the resulting expression leads to the equation

$$\frac{N^*_{\mathrm{N_2O}}}{N_{\mathrm{H_2O}} - N^*_{\mathrm{N_2O}}} = \frac{k'_{\mathrm{E}}}{2k'_{\mathrm{c}}}$$

A number of assumptions have been made in the derivation of this expression, and these will now be considered.

(i) It has been tacitly assumed that isotope effects can be neglected. This assumption is commonly made in studies of the kinetics of oxygen-exchange reactions with oxygen-18 as tracer, and does not appear to introduce a significant error. (ii) It has been assumed that $N_{\mathrm{H_2O}}$ remains constant during the exchange; this is justified because in the present work there was always at least a 500-fold excess of oxygen in the form of water over oxygen in the form of nitrite. (iii) The rate equation for chemical reaction was taken as $v = k'_{\mathrm{c}}[\text{nitrite}]$. The kinetic studies described in Parts I and II [1] show that the rate equation under the conditions of the present study is of the first order in nitrite. In all experiments save one (No. 50, Table 3) there was at least a tenfold excess of azide over nitrite, and in all cases there was a large excess of buffering agent over nitrite save in experiment 19, Table 1. (iv) It has been assumed that reaction was complete when the nitrous oxide was removed for isotopic analysis. In all experiments the reacting solutions were left for at least ten half-lives of decomposition before removing the nitrous oxide. There is no exchange between water and nitrous oxide.[9]

EXPERIMENTAL

Materials.—Water enriched in oxygen-18, obtained by fractional distillation of water, was purified by distillation from alkaline permanganate. Sodium nitrite enriched in oxygen-18 was obtained by exchange of the isotopically normal salt with [^{18}O] water of *ca.* 2% enrichment.[3] The preparation and purification of the other materials have already been described.[1b]

Isotopic Experiments.—The two solutions were placed in the arms of a Y tube, and frozen by cooling in liquid air. The tube was pumped out, and the frozen solution allowed to warm and melt. The tube was then immersed in an ice–water bath until temperature equilibrium was attained. The contents of the two arms were then rapidly mixed, and the tube kept at 0° for at least ten half-lives. The solutions were again frozen in liquid air, and all non-condensable gas pumped off. The tubes were then allowed to warm and the nitrous oxide was transferred to another vessel, and stored over concentrated sodium hydroxide solution. This removed any small amounts of carbon dioxide; these would interfere with the mass-spectrometric analysis

[9] Friedman and Bothner-By, *J. Chem. Phys.*, 1952, **20**, 4591.

of nitrous oxide. The abundance of oxygen-18 in the nitrous oxide was determined from the relative intensities of the peaks of mass number 44 and 46.

Anbar and Taube have reported that when solutions of sodium nitrite and sodium azide are acidified there is much extraneous exchange between nitrite and solvent.[2] We had similar difficulties. For the decompositions carried out in azide buffers it was necessary to put a solution of isotopically normal sodium nitrite in normal water in one arm of the Y tube, while the enriched water was in the other arm. If the initially normal nitrite was dissolved in enriched water at the start of the experiment, inconsistent results were obtained. This effect was in part due to spraying from one arm to the other during the freezing down and melting processes; also the volatile hydrazoic acid may have distilled over. Both these effects would acidify the sodium nitrite solution, and cause exchange, before the main bulks of the two solutions were mixed. Another effect that might account for some of the inconsistent results is that addition of acid to a solution of sodium nitrite and azide could cause local high concentration of acid and increase the rate of exchange. The work described above has shown that the ratio of exchange rate to reaction rate is much higher in excess of perchloric acid ($[H^+]$ *ca.* 0·2M) than in azide buffers ($[H^+]$ *ca.* 10^{-5}M).

In the experiments with excess of perchloric acid and isotopically normal water these difficulties were not encountered. For these, perchloric acid was in one arm of the Y tube, and enriched sodium nitrite and sodium azide in normal water in the other. The solutions were degassed without freezing, to prevent spraying. Perchloric acid is involatile in dilute aqueous solution, so that there was no distillation from one arm to the other. On mixing the solutions any local concentration of acid was not much higher than those in the final solution, and so the ratio of exchange to chemical reaction was not seriously affected. The final justification for the validity of these methods is to be found in the good agreement between the rate of the nitrous acid–water exchange obtained from reaction in azide buffers at pH 4—5, in excess of perchloric acid at pH 1—2, and from the direct measurements of the exchange rate which make no assumptions about the mechanism of the azide–nitrite reaction, but use it essentially as an empirical analytical method.

The authors are indebted to Professor E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for their interest and to Dr. J. H. Ridd for many valuable discussions.

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[*Received, April 27th,* 1959.]