116. *Oxygen Exchange between Nitrous Acid and Water.*

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The rate of exchange of oxygen atoms between water and nitrous acid is proportional to the square of the concentration of nitrous acid. This second-order rate law corresponds to the formation of dinitrogen trioxide, with consequent oxygen exchange. The rate of formation of dinitrogen trioxide, estimated from the rate of oxygen exchange, is similar to that estimated from the rate of diazotisation of aniline.

THERE are many reactions of nitrous acid (or its esters) in which there is nucleophilic attack upon the nitrogen atom, with expulsion of a hydroxyl (or alkoxyl) group. These reactions do not occur in alkaline solution (except for the esters). Thus the nitrite ion does not exchange its oxygen atoms with water,[1] but the nitrous oxide from the decomposition of nitrous acid by hydroxylamine in $H_2{}^{18}O$ is isotopically enriched;[2] therefore there must be oxygen exchange between water and nitrous acid, or some entity derived from the latter.

There are various possible reaction paths for this exchange:

$$(1)\quad H_2\overset{+}{N}O_2 + H_2{}^{18}O \rightleftharpoons H_2\overset{+}{N}O_2{}^{18}O + H_2O$$

$$(2)\quad H_2\overset{+}{N}O_2 \rightleftharpoons \overset{+}{N}O + H_2O$$

$$(3)\quad H_2\overset{+}{N}O_2 + N\overset{-}{O}_2 \rightleftharpoons N_2O_3 + H_2O$$

Reactions analogous to (1) are the acid-catalysed hydrolyses of alkyl nitrites[3] and the acid-catalysed diazotisation of aromatic amines by the nitrous acidium ion.[4] Reaction (2) must occur in concentrated mineral acid, because the nitrosonium ion ^{+}NO exists in such solutions.[5] Diazotisation and deamination by dinitrogen trioxide, formed by reaction (3), are also well known.[6]

Many reactions of nitrous acid and its esters are catalysed by nucleophilic anions, so we studied the oxygen exchange of nitrous acid in the absence of such anions (with the necessary exception of nitrite). There being no net chemical change during an isotopic exchange, it is easy to control the acidity of a solution without recourse to a buffer. Here small amounts of perchloric acid were added to a large excess of sodium nitrite; the concentration of nitrous acid was then that of the added perchloric acid. Preliminary accounts of this work have been given.[7]

Various methods can be devised for following the oxygen exchange between nitrous acid and water. The simplest is to follow the changing isotopic abundance of the water.[1]

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[1] Alexander and Hall, *J. Amer. Chem. Soc.*, 1940, **62**, 3455.
[2] Friedman and Bothner-By, *J. Chem. Phys.*, 1952, **20**, 459.
[3] Allen, *J.*, 1954, 1968.
[4] Hughes, Ingold, and Ridd, *J.*, 1958, 77.
[5] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **149**, 327; **150**, 615; Bayliss and Watts, *Austral. J. Chem.*, 1956, **9**, 319; Singer and Vamplew, *J.*, 1956, 3971; Gillespie and Millen, *Quart. Rev.*, 1948, **2**, 277.
[6] (*a*) Hughes, Ingold, and Ridd, *J.*, 1958, 65, 70, 88; (*b*) Taylor, *J.*, 1928, 1099, 1897.
[7] Bunton, Llewellyn, and Stedman, *Nature*, 1955, **175**, 83; *Chem. Soc. Spec. Publ.*, 1957, No. 10, 113.

Alternatively, the nitrous acid can be decomposed *in situ* by reagents such as hydroxylamine [2] or hydrazoic acid [8] to a gas, *e.g.*, nitrous oxide, which can be analysed mass spectrometrically. As control tests on the azide method showed that some oxygen of the nitrous oxide came from the water during decomposition, we did not use this method, although others have used it successfully.[8] Our usual method was the isolation of nitrous acid as its silver salt, and decomposition of this to water by heating it with ammonium chloride. The first method, analysis of the solvent water, was used for a few experiments. The concentration of nitrite was varied between 0·4 and 3M.

At 0° in water, the rate of exchange R was proportional to the square of the nitrous acid concentration, and independent of the stoicheiometric concentration of nitrite (Table 1), *i.e.*, $R = k_{ex}[HNO_2]^2$. Therefore the most plausible scheme for this exchange (in the absence of other anions) is:

TABLE 1. *Oxygen exchange between nitrous acid and water at* 0°.

10[HNO$_2$] (M)	[Nitrite] (M)	10^3R (mole l.$^{-1}$ sec.$^{-1}$)	$10R/[HNO_2]^2$ (l. mole^{-1} sec.$^{-1}$)	10[HNO$_2$] (M)	[Nitrite] (M)	10^3R (mole l.$^{-1}$ sec.$^{-1}$)	$10R/[HNO_2]^2$ (l. mole^{-1} sec.$^{-1}$)
0·118	0·555	0·0582	4·2	0·541	1·995	1·34	4·6
0·133	0·412	0·104	5·8	0·561	1·087	1·41	4·5
0·258	0·410	0·410	6·2	0·561	0·517	1·71	5·4
0·258	0·655	0·297	4·5	0·792	0·591	3·80	6·0
0·264	0·536	0·319	4·6	1·13	0·457	7·46	5·8
0·287	1·134	0·368	4·5	0·177 *	2·76	0·173	5·5
0·352	1·162	0·575	4·7	0·0765 †	1·40	0·294	50
0·376	0·534	0·796	5·6	0·231 †	1·40	3·55	67

Mean $R/[HNO_2]^2 = 0{\cdot}51$ (l. mole^{-1} sec.$^{-1}$) at 0°.

* Method 2 used. † 25·0°.

$$2HNO_2 \rightleftharpoons H_2\overset{+}{N}O_2 + \overset{-}{N}O_2 \text{ (fast)}; \quad H_2\overset{+}{N}O_2 + \overset{-}{N}O_2 \rightleftharpoons N_2O_3 + H_2O$$

Paths (1) and (2) would give the law

$$R = k[H^+][HNO_2] \approx k'[HNO_2]^2/[NO_2^-]$$

These paths cannot be major mechanistic components because of the independence of rate of the concentration of nitrite ion. They may be important in conditions other than those used here.

Our solutions always contained perchlorate ion from the acid, and small amounts of nitrate ion from the added nitrite. Addition of small amounts (<0·1M) of these ions did not affect the exchange rates (Table 2).

TABLE 2. *Effect of added salts of strong acids* (Method 1).

	Added salt (M)	10[HNO$_2$] (M)	[Nitrite] (M)	10^3R (mole l.$^{-1}$ sec.$^{-1}$)	Rate increase (%)
NaClO$_4$	0·072	0·302	0·601	0·451	−3
,, ...	1·02	0·500	0·819	2·21	41
NaNO$_3$	0·055	0·245	0·555	0·251	−17
,, ...	0·197	0·451	0·620	1·00	−4
,, ...	1·32	0·257	0·829	0·487	42
,, ...	1·37	0·537	0·564	2·43	62
NaCl	2·16	0·240	0·788	0·657	119
,, ...	2·21	0·354	0·762	1·39	114
NaBr	1·02	0·190	0·660	0·315	68
,, ...	1·21	0·184	0·661	0·352	99
KCNS	1·45	0·211	0·796	0·415	79

Comparison with the Hydrolysis of Alkyl Nitrites.—The exchange of oxygen between water and carboxylic acids is analogous to hydrolysis of their esters, so we might expect a similar correspondence between nitrous acid exchange and alkyl nitrite hydrolysis. The mechanism of the acid hydrolysis of alkyl nitrite is a bimolecular attack of water upon the

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

conjugate acid of the ester.[3] We have not observed this mechanism for the oxygen exchange of nitrous acid. This is not necessarily because it does not exist; it may be that, with the large concentration of nitrite ion used the bulk reactivity of nitrite ions towards nitrous acidium ion is much greater than that of water. From the known rates of hydrolyses of alkyl nitrites we can calculate the relative reactivities of halide ions and water towards a protonated alkyl nitrite. For *n*-propyl nitrite in aqueous dioxan $k_{H_2O}/k_{Br^-} \approx 5 \times 10^{-4}$, and because nitrite and bromide ions have similar reactivities towards the nitrous acidium ion [6a, 9] the ratio $k_{H_2O}/k_{NO_2^-}$ for attack upon the protonated ester is probably not very different. If the relative reactivities of nitrite ion and water towards the nitrous acidium ion and protonated ester are similar it will therefore be possible to observe exchange *via* bimolecular attack of water as an isolated mechanism only when the concentration of nitrite ion is much less than that used here.

Comparison with Diazotisation.—In many reactions dinitrogen trioxide is the reactive intermediate, and for some of these, *e.g.*, the diazotisation of aniline, its formation can be rate-determining.[6a] Then the kinetic form becomes Rate $= k''_2[\mathrm{HNO_2}]^2$. The two measurements were made under very different conditions (for diazotisation $[\mathrm{NO_2^-}] \approx 10^{-3}$M) and the estimated value [6a] of k''_2 (but not of k_{ex}) depends upon the value taken for the dissociation constant of nitrous acid. Within these limitations there is fair agreement between k_{ex} and k''_2, *e.g.*, at 0° in water, $k_{ex} = 0{\cdot}51$ (l. mole^{-1} sec.$^{-1}$) [$k''_2 \approx 0{\cdot}8$ (l. mole^{-1} sec.$^{-1}$)].

Effect of Added Anions.—Added anions, X^-, may affect the rate of exchange in two ways: (*a*) they may have a primary or secondary salt effect, or (*b*) they may provide a new path for oxygen exchange, *e.g.*,

$$\mathrm{H_2\overset{+}{N}O_2} + \overset{-}{\mathrm{X}} \rightleftharpoons \mathrm{NOX} + \mathrm{H_2O}$$

The second mode must play a part whenever the bulk reactivity of the added anion towards the nitrous acidium ion is comparable with that of the nitrite ion.

Anions of Weak Acids.—In solutions of nitrous acid buffered with phosphate or carboxylate ions attack of these highly nucleophilic anions may swamp the uncatalysed attack of nitrite ion. Then the rate of exchange will be of the first order with respect to nitrous acid, and will depend upon the nature and concentration of the buffer. This seems to occur with acetate buffers, because here the rate of exchange, at a given pH, is approximately proportional to the first, not the second, power of the nitrite concentration (Table 3 and ref. 7). Such a catalysis almost certainly also occurs with phosphate buffers, although it is here complicated by the coexistence of mono- and di-anions, which will have different reactivities towards the nitrous acidium ion.

TABLE 3. *Exchange in acetate buffer at* 25° (Method 2).

[Nitrite] (M)	$[\mathrm{CH_3{\cdot}CO_2Na}]$ (M)	$[\mathrm{CH_3{\cdot}CO_2H}]$ (M)	pH *	10^4R (mole l.$^{-1}$ sec.$^{-1}$)
0·560	3·92	1·48	5·32	4·7
1·61	3·79	1·44	5·36	10·3

* Measured with a glass electrode.

TABLE 4. *Thiocyanate-catalysed diazotisation of aniline at* 0°.

$10^2[\mathrm{PhNH_2,HClO_4}]$ (M)	0·98	3·93	0·98	0·98	1·97
$10^3[\mathrm{H^+}]$ (M)	2·57	2·57	2·57	3·17	6·14
$10^3\{[\mathrm{HNO_2}] + [\mathrm{NO_2^-}]\}$ (M)	1·00	1·00	1·00	0·40	1·00
$10^4[\mathrm{C\overset{-}{N}S}]$ (M)	9·41	9·41	3·76	9·41	3·76
$10^6 \times$ Instantaneous rate	2·55	2·55	1·33	0·82 *	2·75
$10^{-3}k_3^{\mathrm{CNS}}$	1·37	1·37	1·54	1·45	1·55

* Instantaneous rates were calculated at a point of the run corresponding to $10^4\,[\mathrm{HNO_2}] = 6{\cdot}67$M, except for run *; here the rate refers to $10^4\,[\mathrm{HNO_2}] = 1{\cdot}82$M.

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[9] Hughes, Ingold, and Ridd, *J.*, 1958, 82.

Effect of Anions of Strong Acids.—Halide ions catalyse diazotisation, and the acid hydrolysis of alkyl nitrites, by introducing new paths, *viz.*,

$$H_2\overset{+}{N}O_2 + \overset{-}{Br} \rightleftharpoons NOBr + H_2O; \quad RO\overset{+}{N}OH + \overset{-}{Cl} \rightleftharpoons NOCl + ROH$$

The nitrosyl halide then reacts with a nucleophilic reagent, *e.g.*, water or amine.[9] The relative reactivities of halide and nitrite ions towards the nitrous acidium ion can be calculated from rates of diazotisation [6a, 9] (in the Experimental section we give results on rates of diazotisation which give an estimate of the relative reactivity of the thiocyanate ion also). These diazotisations are made at low ionic strengths, where specific salt effects are relatively unimportant. Nucleophilic anions (*e.g.*, Br^-, CNS^-) catalyse diazotisation, but the weakly nucleophilic anions (*e.g.*, NO_3^- and ClO_4^-) have little effect when in low concentration. In principle it should be possible to do similar experiments on oxygen exchange. Unfortunately our experimental methods required concentrations of nitrite ion $>0{\cdot}4$M, and so to get an accurately measurable increase in rate it was necessary to use even higher concentrations of the added salt. Preliminary experiments showed that such high salt concentrations had a marked effect on diazotisation, and this has since been confirmed by a more detailed study.[10]

Added sodium perchlorate, nitrate, bromide, and chloride and potassium thiocyanate (1—2M) increased the rate of oxygen exchange, *e.g.*, the rate was doubled in the presence of 2M-sodium chloride (Table 2). These effects depended upon the nature and concentration of the added salt. The sequence was: $NaBr > KCNS \approx NaCl > NaClO_4 > NaNO_3$. These rate increases could be caused by either a chemical intervention, or specific salt effects, or both. It did not seem possible to separate these effects at the high salt concentrations used.

Sodium nitrite itself appears to have no specific salt effect upon the rate of exchange, which is unaffected by an eightfold change in the concentration of sodium nitrite (Table 1). We therefore think that the rates of diazotisation and oxygen exchange can be compared despite the considerable differences in the concentration of nitrite ion.

The rate of dehydration of nitrous acid to dinitrogen trioxide can be written as:

$$\text{Rate} \propto [HNO_2]^2 f^2_{HNO_2}/f^*$$

(where f_{HNO_2} and f^* are the activity coefficients of nitrous acid and the transition state respectively).

We might expect the activity-coefficient term to cancel out, because the transition state is made up of two molecules of nitrous acid. This seems to be so when sodium nitrite is the only salt present in high concentration. However, salt effects are often highly specific, and it may be that the term $f^2_{HNO_2}/f^*$ will change when salts other than sodium nitrite are present in large amounts. f_{HNO_2} changes only slowly with ionic strength,[11] and so variation in the activity coefficient term is probably largely due to changes in f^*.

EXPERIMENTAL

Kinetic Methods for Isotopic Exchange.—(1) *Determination of isotopic abundance of nitrous acid.* Decomposition of isotopically normal nitrous acid in $H_2{}^{18}O$ by hydrazoic acid or hydroxylamine gave some tracer in the nitrous oxide; the amount depended upon the conditions used. It seems, however, that the azide method can give reproducible results under standard conditions (cf. ref. 8). Decomposition of the nitrous acid, or its salts, to nitric oxide was not a satisfactory method, in part because the gas causes difficulties in mass spectrometry.[12]

Therefore the nitrous acid was isolated as its sparingly soluble silver salt, and this was decomposed: $AgNO_2 + NH_4Cl \longrightarrow N_2 + 2H_2O + AgCl$. The water was equilibrated with carbon dioxide and this gas analysed mass spectrometrically. (This method could not be used when a salt or acid giving an insoluble oxygen-containing silver salt was present.)

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[10] Challis and Ridd, personal communication.

[11] Abel and Neusser, *Monatsh.*, 1929, **53**, 855.

[12] Bigeleisen, *J. Amer. Chem. Soc.*, 1952, **74**, 4944.

The nitrous acid solutions were covered with a layer of purified heptane; this greatly decreased the rate of decomposition of the nitrous acid. Sodium nitrite, sometimes with another salt, in $H_2{}^{18}O$, was cooled to 0°, and oxygen and carbon dioxide were removed in a stream of nitrogen. The required amount of ice-cold perchloric acid was then added (nitric acid was used when potassium thiocyanate was present). At suitable times, portions were removed and added to a slight excess of aqueous ammonia (s.g. 0·880). An aliquot part was removed and titrated with standard alkali, in the absence of carbon dioxide, with Thymol Blue indicator. (All solution transfers were made with pre-cooled pipettes.) The excess of ammonia was pumped off from the samples, and silver nitrate added. The washed silver nitrite precipitate was dried *in vacuo* (P_2O_5), then ground with dried ammonium chloride, and all volatile matter was pumped off at room temperature. The mixture was decomposed *in vacuo* at 220°. The evolved water distilled out, and was purified by static distillation. This purified water was then isotopically analysed by means of equilibrated carbon dioxide. A correction was applied for the isotopic dilution by the oxygen atoms of the carbon dioxide.

We tested the validity of this method. (1) Isotopically normal sodium nitrite was added to ammonia in $H_2{}^{18}O$. The isolated silver nitrite contained no tracer. (2) Silver nitrite did not exchange with $H_2{}^{18}O$ either in the presence or absence of silver nitrate. (3) An isotopic dilution experiment showed that no significant amounts of tracer were introduced *via* the reagents. (4) The isotopic abundance of the nitrite, found and calculated for complete exchange, agreed within 5%. This difference may be due to adventitious loss of tracer, or to isotopic fractionation. The value of isotopic abundance for complete exchange, N_∞, was taken as that calculated from the isotopic abundance of the water, and the relative amounts of water and sodium nitrite.

(2) *Determination of the changing abundance of the water.* Isotopically enriched sodium nitrite was prepared by equilibration with $H_2{}^{18}O$ containing a trace of nitric acid. After several days the water was pumped off, and the salt dissolved in normal water, and redried *in vacuo*. This was repeated. The dried and powdered salt, stored *in vacuo* (P_2O_5), contained more than 99·5% of sodium nitrite (w/w). Solutions of this enriched salt were made up with isotopically normal water containing perchloric acid or acetate buffer, as for Method 1. At intervals samples were removed, and the exchange stopped by addition of a small known amount of sodium hydroxide. The water was pumped off and analysed by use of equilibrated carbon dioxide. Corrections were made for isotopic dilutions during analysis. This method was used for a run with phosphate buffer (0·05M, pH 5·39) and 0·664M-sodium nitrite at 25°; $10^5R = 4{\cdot}0$ (mole l.$^{-1}$ sec.$^{-1}$). This value is close to that found by Anbar and Taube [8] for exchange in a similar buffer (pH 5·47) and 0·50M-sodium nitrite, *viz.*, $10^5R = 3{\cdot}5$ (mole l.$^{-1}$ sec.$^{-1}$).

Calculation of Results.—The exchange rate R was calculated from:

$$R = \frac{2[\text{nitrite}][H_2O]}{2[\text{nitrite}] + [H_2O]} \cdot \frac{d \log_e (N_\infty - N_t)}{dt}$$

N_t and N_∞ are the isotopic abundances in excess at time t and for complete exchange respectively.

Exchange in $H_2{}^{18}O$. [Nitrite] = 0·591M. [HNO_2] = 0·0792M. 0°

Time (min.)	1·50	3·06	5·03	7·50	∞		
N (atoms % excess)	0·434	0·515	0·738	0·834	1·066	1·049	1·063*

* Calc. from N_{H_2O}.

$10^3R = 3{\cdot}80$ moles l.$^{-1}$ sec.$^{-1}$; $R/[HNO_2]^2 = 0{\cdot}603$ l. mole^{-1} sec.$^{-1}$.

Exchange with $NaNO^{18}O$. [Nitrite] = 1·40M. [HNO_2] = 0·023M. 25°.

Time (min.)	1·14	2·02	3·02	5·58	8·03	∞		
N (atoms % excess)	0·027	0·029	0·042	0·090	0·098	0·242	0·241	0·242

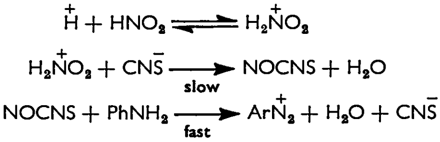
$10^3R = 3{\cdot}55$ moles l.$^{-1}$ sec.$^{-1}$; $R/[HNO_2]^2 = 6{\cdot}68$ l. mole^{-1} sec.$^{-1}$.

Appendix.—Catalysis of diazotisation by thiocyanate ion. It was found that potassium thiocyanate (*ca.* M) increased the rate of oxygen exchange between nitrous acid and water (Table 2). This could be a salt effect, or the result of the new reaction path:

$$CNS^- + HNO_2{}^+ \rightleftharpoons NO{\cdot}CNS + H_2O$$

Nitrosyl thiocyanate might well be a nitrosating agent, as are the nitrosyl halides. Therefore the diazotisation of aniline was studied with added potassium thiocyanate at 0° in water, following the procedures already described.[4, 6a, 9]

In the absence of added thiocyanate ion the rate equation is $v = k''_2[HNO_2]^2$, corresponding to the rate-determining formation of dinitrogen trioxide.[6a] Addition of thiocyanate ion increased the rate, which was independent of a change in concentration of amine from 0·01M to 0·04M. A series of experiments were made with different reagent concentrations (Table 4). Instantaneous rates were calculated by drawing tangents to the concentration–time curve at *ca.* 20% reaction. These were corrected for the uncatalysed rate of diazotisation through dinitrogen trioxide, the dissociation constant of nitrous acid being taken as $3{\cdot}2 \times 10^{-4}$ mole l.$^{-1}$ at 0°, to give the rate of formation of nitrosyl thiocyanate $= k_3^{ONS}[H^+][HNO_2][\overset{-}{CNS}]$. From these figures, $10^5 k_3^{ONS} = 1{\cdot}5$ l.^{2} mole^{-2} sec.$^{-1}$ for the overall reaction:



$$\overset{+}{H} + HNO_2 \rightleftharpoons H_2\overset{+}{N}O_2$$

$$H_2\overset{+}{N}O_2 + \overset{-}{CNS} \xrightarrow[\text{slow}]{} NOCNS + H_2O$$

$$NOCNS + PhNH_2 \xrightarrow[\text{fast}]{} Ar\overset{+}{N}_2 + H_2O + \overset{-}{CNS}$$

and k_3^{ONS} is a measure of the reactivity of the thiocyanate towards the nitrous acidium ion. Its value is very similar to those found for the iodide ($10^5 k_3^{I} = 1{\cdot}4$ l.^{2} mole^{-2} sec.$^{-1}$) and bromide ions ($10^5 k_3^{Br} = 1{\cdot}2$ l.^{2} mole^{-2} sec.$^{-1}$).[9]

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