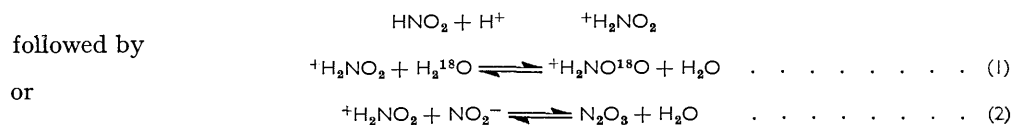


57. Oxygen Exchange between Nitrous Acid and Water.
Part II.* Exchange in Acetate Buffers.

By C. A. BUNTON and M. MASUI.

Acetate ions catalyse the exchange of oxygen atoms between nitrous acid and water. The rate law is $R \propto [\text{HNO}_2][\text{H}^+][\text{OAc}^-]$. The mechanism is thought to be attack of acetate ions on the nitrous acidium ion with formation of nitrosyl acetate. Competition experiments, in the absence of acetate buffer, show that dinitrogen trioxide, formed from two molecules of nitrous acid, is captured rapidly by aniline, and that oxygen exchange between nitrous acid and water (by formation and rehydration of dinitrogen trioxide) is thus suppressed.

It is known (from Part I * and ref. 1) that nitrous acid and water can exchange oxygen atoms in solutions which contain no nucleophilic anions (other than nitrite) by two mechanisms which can be written:



These mechanisms of oxygen exchange can be compared with known mechanisms of such reactions as diazotisation,² the hydrolysis of alkyl nitrites,³ and the decomposition of nitrous acid by hydrazoic acid.⁴ These reactions are catalysed by nucleophilic anions, and hence by most buffers. Our present work is a study of oxygen exchange in presence of a buffer. Anbar and Taube⁵ already studied the exchange of oxygen atoms between water and nitrous acid in phosphate buffers, but they did not separate the buffer-catalysed and the buffer-independent components of the exchange: it would be very difficult to do this, because the various phosphate ions will have different nucleophilic powers.

The rates of oxygen exchange between water and nitrous acid in acetate buffer at 0°.

pH	4.60	4.62	4.99	5.20	5.27	5.31	5.39	5.40	5.43	5.60	5.95
[NO ₂ ⁻] (M)	0.056	0.037	0.058	0.039	0.066	0.165	0.040	0.025	0.066	0.040	0.040
[HOAc] (M)	0.75	0.67	0.25	0.33	0.167	0.167	0.093	0.083	0.330	0.200	0.050
[OAc ⁻] (M)	0.25	0.33	0.25	0.67	0.333	0.333	0.167	0.167	0.670	0.800	0.450
10 ⁵ (R mole l. ⁻¹ sec. ⁻¹) } obs.	26.7	10.5	2.59	1.38	0.985	2.47	0.351	0.200	1.62	0.338	0.067
} corr.	22.6	8.6	1.98	1.24	0.825	2.25	0.288	0.171	1.56	0.324	0.065

We chose acetate buffers for our present work because earlier experiments had shown that the rate of oxygen exchange in acetate buffers had a first-order dependence upon the concentration of nitrous acid,^{1a} and that hydrolysis of the intermediate nitrosyl acetate is by fission of the nitrogen-oxygen bond.⁶ The concentration of "nitrite" was 0.025—0.165M (by "nitrite" we mean the species which give nitrous acid when diluted with water). Because we desired the buffer-catalysed exchange to be much faster than the uncatalysed exchange, the concentration of acetate buffer was always appreciably greater than that of "nitrite." The results of the exchange experiments are given in the Table. Correction is made for the amount of uncatalysed exchange (cf. Part I and ref. 1b); for all runs this correction is small.

* *J.*, 1959, 568, is regarded as Part I.

¹ (a) Bunton, Llewellyn, and Stedman, *Chem. Soc. Spec. Publ.*, 1957, No. 4, p. 113; (b) Bunton and Stedman, *J.*, 1959, 3466.

² Hughes, Ingold, and Ridd, *J.*, 1958, 77, and accompanying papers.

³ Allen, *J.*, 1954, 1968.

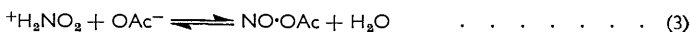
⁴ Stedman, *J.*, 1959, 2943; Seel, Wölfe, and Zwarg, *Z. Naturforsch.*, 1958, 13b, 136.

⁵ Anbar and Taube, *J. Amer. Chem. Soc.*, 1955, 77, 2993.

⁶ Stedman, Thesis, London, 1955.

For a given pH and buffer concentration the rate of exchange is proportional to the concentration of "nitrite" (see, *e.g.*, the experiments at pH 5.27 and 5.31, and at pH 5.39 and 5.40).

At a given pH the exchange is considerably faster than in the absence of acetate buffer. From the explanation given to the rates of diazotisation in acetate or phthalate buffers,² we would expect oxygen exchange to be by the reaction



which is analogous to (2).

This would give the kinetic form:

$$R = k^{\text{OAc}^-} [\text{H}^+] [\text{HNO}_2] [\text{OAc}^-] \quad \dots \quad (I)$$

This expression can be rearranged in various approximate forms, *e.g.*:

$$\frac{R}{[\text{NO}_2^-]} = \frac{k^{\text{OAc}^-}}{K_{\text{HNO}_2}} [\text{H}^+]^2 [\text{OAc}^-] \quad \dots \quad (Ia)$$

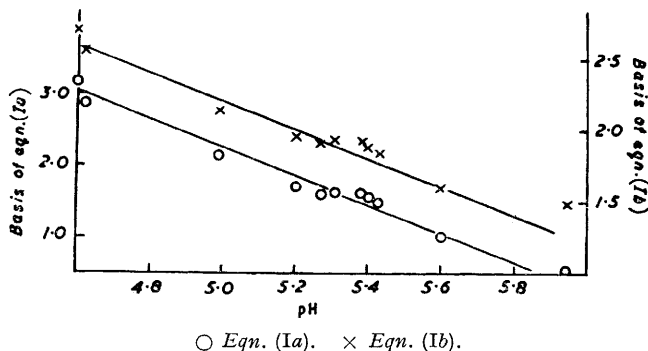
or

$$\frac{R}{[\text{NO}_2^-]} = k^{\text{OAc}^-} \frac{K_{\text{HOAc}}}{K_{\text{HNO}_2}} [\text{H}^+] [\text{HOAc}] \quad \dots \quad (Ib)$$

The equations (Ia and b) are plotted in their logarithmic forms in the Figure (with the approximation $\text{pH} = -\log[\text{H}^+]$). Equation (Ia) requires that a plot of

Exchange between nitrous acid and water in acetate buffer at 0°.

Numerical values on the basis of eqn. (Ia) are $5 + \log (R/[\text{NO}_2^-][\text{OAc}^-])$; and those on the basis of eqn. (Ib) are $5 + \log (R/[\text{NO}_2^-][\text{HOAc}])$.



$\log (R/[\text{NO}_2^-][\text{OAc}^-])$ against pH should have a slope of -2 ; and (Ib) requires that a plot of $\log (R/[\text{NO}_2^-][\text{HOAc}])$ against pH should have a slope of -1 . The respective lines have been drawn with these slopes. Therefore, from our results for the kinetic form (I), using the values $10^4 K_{\text{HNO}_2} = 3.2 \text{ mole l.}^{-1}$,⁷ and $10^5 K_{\text{HOAc}} = 1.66 \text{ mole l.}^{-1}$,⁸ we calculate $10^{-3} k^{\text{OAc}^-} \approx 5 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ from (Ia), and $3 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-2}$ from (Ib). This calculation neglects the effect of ionic strength on the equilibria and reactions involved; and this effect may be appreciable, particularly because we are using thermodynamic dissociation constants. However, the aim of this work was to study the mechanism of this oxygen exchange in the presence of a nucleophilic buffer rather than to obtain a precise value for its rate constant. This could be obtained more conveniently by chemical experiments in more dilute solutions. It is likely that the value of k^{OAc^-} from equation (Ib) is the more reliable because of a cancellation of the salt effects on $K_{\text{HNO}_2}/K_{\text{HOAc}}$.

Using the value of k^{OAc^-} from equation (Ib) we calculate that the acetate ion is less than twice as reactive as is nitrite ion² towards the nitrous acidium ion. Thus it has a reactivity

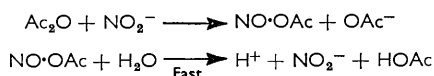
⁷ Klemenc and Hayek, *Monatsh.*, 1929, **54**, 407.

⁸ Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652.

similar to those of a large number of nucleophilic anions,^{2,4} in accord with the observation that the nitrous acidium ion discriminates little between reagents of similar charge.

Our experiments, by themselves, do not prove that the exchange is by attack of acetate ions upon the nitrous acidium ion; either a bimolecular reaction between nitrous and acetic acids or a termolecular reaction between nitrous acid, acetate ion, and a proton would have the same kinetic form as reaction (3). We use the formulation of a nucleophilic substitution upon the nitrous acidium ion because of the similarity between this reaction and other reactions of nitrous acid which are so formulated.

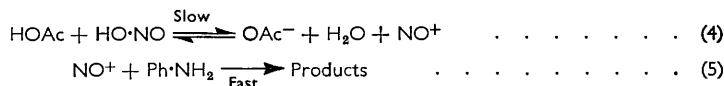
Other reactions in which formation of nitrosyl acetate seems to be of kinetic importance are the reaction between nitrous and hydrazoic acids^{1a,4} and the diazotisation of amines.^{2,9} In these reactions the nitrosyl acetate is probably formed by reaction between nitrous acidium and acetate ions. There appears to be another route for its formation, which is important in the catalysis by nitrite ion of the hydrolysis of acetic anhydride, namely:¹⁰



Our results do not agree with the interpretation which Edwards and his co-workers⁹ have given to the kinetics of diazotisation of aniline in acetate buffers. These authors suggest that the rate equation is made up of several terms of which the most important is:

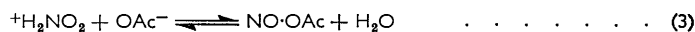
$$\text{Rate} = k^{\text{OAc}^-}[\text{NO}_2^-][\text{OAc}^-][\text{H}^+]^2 \quad \dots \quad (\text{II})$$

This term is thought to represent the kinetics of the following reactions:

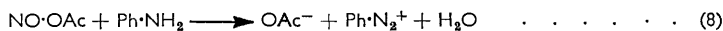


If this interpretation is correct the rate of diazotisation of aniline should be greater than, or at least equal to, the rate of oxygen exchange in the same acetate buffer. We cannot make a precise comparison between the rates of diazotisation and oxygen exchange, because different concentrations of buffer were used. Edwards and his co-workers quote, for the diazotisation of aniline at 0°, a rate of 24.8×10^{-7} mole l.⁻¹ sec.⁻¹ with $[\text{HOAc}] + [\text{OAc}^-] = 0.20\text{M}$ and $[\text{NaNO}_2] = 0.08\text{M}$ at pH 5. The rate of oxygen exchange at 0° is 259×10^{-7} mole l.⁻¹ sec.⁻¹, with $[\text{HOAc}] + [\text{OAc}^-] = 0.50\text{M}$ and $[\text{NaNO}_2] = 0.06\text{M}$ at pH 4.99 (see Table). Thus the rate of exchange, calculated for the conditions of the diazotisation experiment, is *ca.* 130×10^{-7} mole l.⁻¹ sec.⁻¹, *i.e.*, five times that of diazotisation. It is improbable that such a small change in the concentrations could affect the rate so much. Reaction (4) which is supposed to form the nitrosonium ion⁹ requires that the rate of diazotisation should be not less than that of oxygen exchange; we therefore suggest that the kinetic scheme (4) and (5) be modified.

Our experimental results are consistent with an alternative interpretation of the buffer-catalysed diazotisation of an aniline.² In this work the order with respect to "nitrite" was *ca.* 1.7 for the acetate-catalysed reaction. This was explained by the reactions:



together with a reaction which was of the first order with respect to "nitrite"; this could perhaps be:



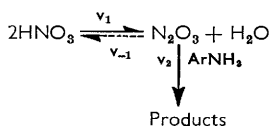
⁹ Edwards, Abbott, Ellison, and Nyberg, *J. Phys. Chem.*, 1959, **63**, 359.

¹⁰ Lees and Saville, *J.*, 1958, 2262.

This kinetic scheme requires that the rate of oxygen exchange, by reaction (3), is greater than that of diazotisation, in agreement with experiment.

Because the nitrous acidium ion differentiates little between various nucleophilic reagents, it is possible to vary the mechanisms of nitrous acid reactions by varying the bulk reactivity of the nucleophilic reagents, usually by varying their concentrations. Similarly, the acetate-catalysed diazotisation will have the rate law (II) when the bulk reactivity of nitrite or aniline towards nitrosyl acetate is greater than that of water, whereas the rate law will approximate to $\text{Rate} \propto [\text{HNO}_2]^2[\text{OAc}^-]$ when the bulk reactivity of nitrite ion towards nitrosyl acetate is less than that of water, but greater than that of aniline.² It should be possible to satisfy either of these conditions by suitable variation of the relative concentrations of the nucleophilic reagents.

A further point has been studied in this work. The observation of a diazotisation which is of second order in nitrous acid and of zero order with respect to the amine indicates that dinitrogen trioxide is formed slowly from two molecules of nitrous acid, and is captured by the amine as rapidly as it is formed,² *i.e.*:



i.e., $v_2 \gg v_{-1}$.

Thus aniline should suppress the exchange of oxygen atoms by formation and hydration of dinitrogen trioxide. An experiment on these lines was made by Anbar and Taube,⁵ who found that this exchange was not suppressed by aniline in solutions containing acetate buffer. This is readily explicable,² because the reactions involved are 3, 6, and 7 (p. 306). Aniline (in low concentration) did not apparently react sufficiently rapidly with nitrosyl acetate to suppress the hydrolysis back to nitrous acid, so that oxygen exchange will occur by reaction (3) even when the rate of diazotisation is independent of amine concentration.²

To avoid these complications we studied the oxygen exchange between nitrous acid and water in solutions which contained only sodium nitrite, nitrous acid, aniline, and a small amount of sodium perchlorate. The pH was sufficiently high for oxygen exchange by direct attack of water to be insignificant. (This is a necessary precaution because aniline could not suppress the exchange if, as would be expected, the nitrous acidium ion is in equilibrium with nitrous acid.) We found that $\sim 0.02\text{M}$ -aniline completely suppressed the oxygen exchange of a solution of sodium nitrite at pH ~ 6.3 at 0° ; in the absence of aniline we calculate that the "nitrite" would have exchanged *ca.* 10% of its oxygen during the time of the experiment (96 hr.). Thus the results of experiments on the exchange of oxygen atoms between water and nitrous acid in the presence of aniline and in the presence and absence of buffers accord with the conclusions drawn from experiments on diazotisation.²

EXPERIMENTAL

Isotope Exchange.—Kinetic experiments were made with isotopically normal sodium nitrite with water enriched in ^{18}O . The pH was measured by a Doran G pH meter. Materials used were free from carbon dioxide, and the kinetic solution was covered with a layer of spectroscopically pure hexane to decrease the decomposition of nitrous acid. Exchanges were at 0° , and portions of the solution were removed at definite times, the exchange was stopped by addition of alkali, and the nitrous acid decomposed *in vacuo* to nitrous oxide by addition of sodium azide in a phosphate buffer at pH 2. This is the method of Anbar and Taube, and we followed their procedure.⁵ During decomposition there is some exchange between nitrous acid and water (cf. refs. 1 and 5). This exchange is reduced by using a large excess of sodium azide, and its effect decreased by maintaining standard conditions for all decompositions. The nitrous oxide was analysed mass spectrometrically. Using this method we found good agreement with the rate of the uncatalysed exchange determined earlier: with $[\text{NaNO}_2] = 0.66\text{M}$,

$[\text{HNO}_2] = 0.0194\text{M}$, $R/[\text{HNO}_2]^2 = 0.56 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, the mean value of $R/[\text{HNO}_2]^2$ was $0.51 \text{ (l. mole}^{-1} \text{ sec.}^{-1})$ (cf. Part I).

The rate of the oxygen exchange, R , is given by:

$$R = 2[\text{NaNO}_2] (2.3/t) [\log N_\infty / (N_\infty - N_t)]$$

where N_t and N_∞ are the isotopic abundances (above normal) of the "nitrite" at times t and ∞ respectively. The results of an experiment with ["nitrite"] 0.040M , $[\text{HOAc}] 0.050\text{M}$, and $[\text{OAc}^-] 0.450\text{M}$ at pH 5.95 and 0° were:

Time (min.)	1.5	224	360	540	1472	∞
N (atom % excess)	0.135	0.195	0.226	0.293	0.488	0.816
	$10^2 R = 6.7 \text{ mole l.}^{-1} \text{ sec.}^{-1}$.					

Isotopic Exchange in Presence of Aniline.—Several preliminary experiments were made with the following results. The isotopic abundance of nitrous oxide quoted is relative to that of the gas evolved from sodium azide and isotopically normal nitrous acid. Temp. 0° ; $N_{\text{H}_2\text{O}} = 0.95$ atom % excess.

initial	pH	final	$[\text{NaNO}_2]$ (M)	$[\text{HClO}_4]$ (mM)	$[\text{Ph}\cdot\text{NH}_2]$ (mM)	Time (hr.)	$N_{\text{N}_2\text{O}}$
5.90	—		0.05	2.5	9	{ 22	—0.003
						{ 45	—0.002
5.31	6.09		0.055	11.0	20	71	—0.002
6.34	7.28		1.0	2.0	18	90	—0.003

The nitrous acid was analysed isotopically by Anbar and Taube's method.⁵

In the final experiment, at 0° , the initial concentrations were: $[\text{NaNO}_2] 1.0\text{M}$, $10^3[\text{HClO}_4] 2.5\text{M}$, $10^2[\text{Ph}\cdot\text{NH}_2] 1.8\text{M}$, at pH 6.30 . This approximate pH was maintained by regular addition of perchloric acid in enriched water; after 60 hr. aniline sufficient to restore the original concentration was added; after 96 hr. the isotopic abundance of the nitrous acid was -0.002 atom % excess; we estimate that in the absence of aniline there would have been $>10\%$ exchange, *i.e.*, $N_{\text{N}_2\text{O}} > 0.1$ atom % excess.

We thank Professors E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for their interest in this work, and Drs. G. Stedman and J. H. Ridd for many valuable discussions. We are grateful to the Ramsay Memorial Fellowships Trust for a Fellowship to M. M.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, July 16th, 1959.]