

541. *Oxygen Exchange between Nitric Acid and Water. Part III.*
Catalysis by Nitrous Acid.*

By C. A. BUNTON, E. A. HALEVI, and D. R. LLEWELLYN.

The exchange of oxygen between nitric acid and water has been followed isotopically at 0°. In the concentration range 8–28 mole % nitric acid, exchange only occurs in the presence of “nitrous acid.” The kinetic effects of variations in nitric and nitrous acid concentrations have been studied, and are interpreted in terms of a two-stage mechanism, involving exchange between water and nitrous acid, and between nitrous acid and nitric acid.

In an investigation of the exchange of oxygen between nitric acid and water, it was found that, while the direct rate of exchange in aqueous nitric acid containing less than 40 mole % of HNO₃ was too slow to be measurable at 0° (Part I, Bunton, Halevi, and Llewellyn, *J.*, 1952, 4913), the presence of minute amounts of the lower oxides of nitrogen (here given the general name of “nitrous acid”) induces exchange. In the concentration range of nitric acid 8–28 mole %, the exchange can be followed conveniently with nitrous acid concentration 2–12 × 10⁻³ mole %.

The method of following the exchange was similar to that described in Part I, with the modification that “nitrous acid” was either allowed to develop or added as sodium nitrite. The source of the nitrous acid did not affect the experimental results, and the minute amounts of sodium cations had no apparent effect. The nitrous acid was determined during the run, and, as in some runs variations in its concentrations were observed, instantaneous rates of exchange were estimated. As it was found that for a given nitric acid concentration, the instantaneous rate of exchange depended only on the nitrous acid concentration, and not on its source or previous history, we may conclude that the catalysis by nitrous acid does not involve a slow chemical interconversion between the various forms of “nitrous acid,” although it may involve isotopic exchange between these forms.

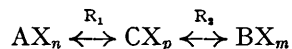
Formal Treatment of Ternary Exchange.—In the present work, as in Part I, the rates, R , of oxygen exchange between nitric acid and water were evaluated from the expression :

$$R = - \frac{3[\text{HNO}_3][\text{H}_2\text{O}]}{3[\text{HNO}_3] + [\text{H}_2\text{O}]} \cdot \frac{d}{dt} (\alpha_\infty - \alpha_t) \quad \dots \quad (1)$$

in which the concentrations are expressed in mole %, and α_∞ and α_t represent the isotopic abundance of ¹⁸O in the nitric acid at complete exchange and at time t , respectively.

Equation (1) was derived for a two-component system, but in exchange catalysed by nitrous acid we must consider, at least formally, two steps in the overall exchange, one between nitrous and nitric acids, and the other involving nitrous acid and water. This does not exclude the possibility that the two steps may be concerted, or that each exchange may involve more than one chemical reaction.

As the system is assumed to be in stoichiometric equilibrium, the exchange reaction may be expressed in terms of two independent exchanges, each involving the nitrous acid catalyst :



We assume that one atom only is transferred per unit act of exchange; then if α , β , and γ are the isotopic abundances of the three species, AX_{*n*}, BX_{*m*}, and CX_{*p*} respectively,

$$n[\text{AX}_n] \cdot (d\alpha/dt) = R_1(\gamma - \alpha) \quad \dots \quad (2a)$$

and

$$-m[\text{BX}_m] \cdot (d\beta/dt) = R_2(\beta - \gamma) \quad \dots \quad (2b)$$

* Part II, *J.*, 1952, 4917.

If the concentration of CX_p is low, the stationary-state treatment gives:

$$R_1(\gamma - \alpha) = R_2(\beta - \gamma) \quad \dots \quad (3)$$

and $n[AX_n] \cdot (d\alpha/dt) = R_1R_2(\beta - \alpha)/(R_1 + R_2) \quad \dots \quad (4)$

and therefore the net rate of exchange R is given in terms of the two component steps by:

$$R = R_1R_2/(R_1 + R_2)$$

Preliminary results on the effect of [nitrous acid] on the overall rate of exchange indicated a variation of kinetic order with respect to [nitrous acid], from 1 to 2, and we assumed a dependency of the form:

i. e., $R_1 = k_1 [“HNO_2”]; R_2 = k_2 [“HNO_2”]^2$
 $R = k_1k_2 [“HNO_2”]^2/(k_1 + k_2 [“HNO_2”]) \quad \dots \quad (5)$

Experimentally the order with respect to [nitrous acid] was estimated by plotting $\log R$ against $\log [nitrous\ acid]$; this pre-supposes that the rate is expressible in the form:

$$R = k [“HNO_2”]^n$$

where n is the order. Obviously equation (5) cannot be expressed in this form and the “kinetic order” as derived by this method has no precise significance except when the order is integral. However this kinetic order is relatively insensitive to small variations in [nitrous acid], and does give an indication of transition from one kinetic form to another.

Our general procedure was to carry out a block of runs at a definite nitric acid concentration, varying the nitrous acid concentration between 2 and 12×10^{-3} mole %. This gave an indication of the apparent kinetic order with respect to [nitrous acid]. The values of the exchange rate interpolated at an arbitrary concentration of 5×10^{-3} mole % of nitrous acid are quoted for the various concentrations of nitric acid. The general procedures for determining the rate and kinetic form of the isotopic exchange are illustrated by Tables 1 and 2. The limiting factor in our kinetic measurements is probably the determination of [nitrous acid], which is carried out colorimetrically after dilution in

TABLE 1.

[HNO ₃] (mole %)	10 ³ [HNO ₂] (mole %)	10 ³ R (mole % sec. ⁻¹)	10 ³ R * (inter- polated) (mole % sec. ⁻¹)	Order	[HNO ₃] (mole %)	10 ³ [HNO ₂] (mole %)	10 ³ R (mole % sec. ⁻¹)	10 ³ R * (inter- polated) (mole % sec. ⁻¹)	Order	
8.2	{ 3.0	0.375	0.62	1.0	23.6	{ 2.7	39.8	122	2.0	
	{ 8.0	0.991				{ 3.8	62.6			
10.5	{ 2.3	0.658	1.72	1.2	25.1	{ 5.5	141	166	1.3	
	{ 6.8	2.49				{ 5.6	173			
16.0	{ 1.9	3.11	13.8	1.6	28.3	{ 3.9	116	179	1.1	
	{ 6.8	23.4				{ 6.7	231			
16.7	{ 4.9	16.0	17.8	1.7	28.3	{ 11.9	462	171	1.1	
	{ 24.0	230				{ 2.2	70.3			
19.7	{ 5.0	39.2	39.5	1.8	28.3	{ 4.8	171	171	1.1	
	{ 9.4	131				{ 4.8	171			
21.8	{ 2.4	20.1	97.8	2.0	* Denotes rate interpolated at [HNO ₂] = 5×10^{-3} mole %.					
	{ 3.0	35.2								
	{ 4.5	82.0								

water (Part I). The effect of this uncertainty, and of the variation in [nitrous acid] is most serious in runs in which the kinetic order tends to second.

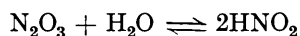
No consideration is given to the mechanism of the nitrous acid decomposition process, and as the rate of exchange depends only on the instantaneous concentration of nitrous acid, and not on its rate of decomposition, the reactions involved in the exchange are not those of the decomposition of nitrous acid.

Discussion.—Any reaction scheme for exchange between water and nitric acid catalysed by nitrous acid must explain the change of kinetic order, with respect to [nitrous

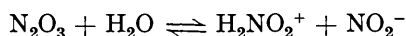
acid], with increasing [nitric acid], from first to second, and back to first above 24 mole % HNO_3 . It must also explain the effect of $[\text{HNO}_3]$ on the overall rate of exchange at fixed [nitrous acid], say 5×10^{-3} moles %. The $[\text{HNO}_3]$ -rate curve shows a sigmoid form, whose exact shape depends on the concentration of nitrous acid arbitrarily chosen (see Fig., lower full curve).

The change of kinetic form with increasing nitric acid concentration may be due to a number of causes: (a) Two independent simultaneous reactions, with different kinetic orders, which depend on acidity. (b) Two consecutive exchange reactions of different kinetic orders, each of which leads to exchange between nitrous acid and one of the other two components. (c) The rate-determining reaction may be of a fixed order with respect to one or other of the nitrous acid species, but its "apparent kinetic order" relative to analytical nitrous acid may vary as a result of the changing relation between the concentrations of the active species and of the total nitrous acid.

The experimental results require that there must at some stage of the exchange be a reaction of the second order with respect to [nitrous acid]. This stage could involve N_2O_4 only in the unlikely event that the bulk component of nitrous acid is NO_2 . The only other species that can reasonably be assumed to participate in a reaction showing second-order kinetics is N_2O_3 , and this only when it is not the bulk component of nitrous acid. Dinitrogen trioxide, exchanging its oxygen with water, by the reaction:

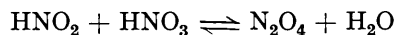


or the kinetically equivalent reaction:



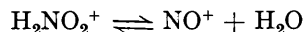
would lead to exchange between nitrous acid and water of rate proportional to $[\text{N}_2\text{O}_3]$.

However, a number of other plausible reactions may be eliminated from consideration. The reaction:



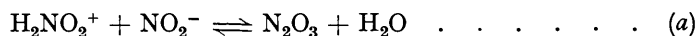
and its protonated equivalent, would lead to a one-step exchange between nitric acid and water, which would be of the first order with respect to [nitrous acid] in all conditions.

Similarly, the formation of the nitrosonium ion by direct ionisation of the nitrous acidium ion by the reaction:

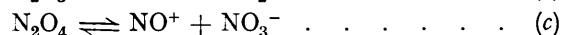
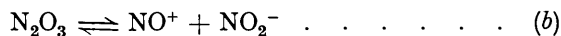


would require a first-order exchange between nitrous acid and water, whose rate would increase indefinitely with increasing acidity. This could not explain the change of kinetic order, and the net rate could be slow only if the reaction $\text{NO}^+ + \text{NO}_3^- \rightleftharpoons \text{N}_2\text{O}_4$, giving exchange between nitrous and nitric acids, were unaffected by increasing nitric acid.

The observed kinetic form is explained by the following exchange sequence:



giving exchange between water and nitrous acid, and exchange between nitrous and nitric acids by the reactions:



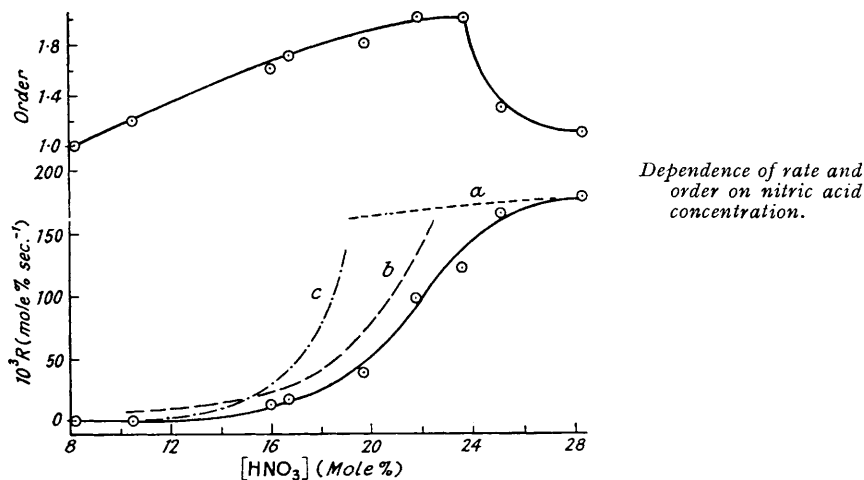
We assume that at low acidities the nitrous acid-water exchange is fast, and that the nitrous-nitric acid exchange by the reactions (b) and (c) is rate determining. If $[\text{N}_2\text{O}_3] \gg [\text{N}_2\text{O}_4]$ the total rate of reaction (c) may be less than that of (b), with reaction (c) the rate-determining step of the exchange. With HNO_2 the bulk component of nitrous acid, reactions (a) and (b), depending on $[\text{N}_2\text{O}_3]$, would both be of second order with respect to [nitrous acid], and reaction (c) is the only reaction which would show this first-order dependence of exchange rate on nitrous acid.

The rates of reactions (b) and (c) should both increase rapidly with an increase of nitric

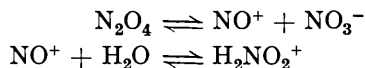
acidity, but protonation of NO_2^- [by decreasing the rate of the back reaction and therefore of the forward reaction of (b)], will make the acid catalysis of (b) less effective than that of (c). The rate of exchange is given by the total number of molecules undergoing reaction, and an increase of the specific rate of (c) may make reaction (b), involving the ionisation of N_2O_3 , the rate-determining step of the exchange, before the concentration of N_2O_4 approaches that of N_2O_3 . The net exchange will then be of first order with respect to $[\text{N}_2\text{O}_3]$, and of second order with respect to [nitrous acid], provided that N_2O_3 is not the bulk component of the nitrous acid.

The exchange between nitrous and nitric acids by reactions (b) and (c), should be continuously acid-catalysed, and the levelling of rate which we observe must be due to reaction (a) becoming rate-determining.

We have assumed that at low acidities the bulk component of nitrous acid is molecular HNO_2 , or its protonated or deprotonated ions, but that in more acid solutions it will be progressively dehydrated to N_2O_3 . The rate of reaction (a) will then no longer increase rapidly, and as N_2O_3 becomes the bulk nitrous acid component, the order will tend towards first.



The experimentally observed variations in rate and kinetic order, with increasing nitric acidity, can therefore be qualitatively reproduced quite simply, as the resultant of the three reactions considered. This is illustrated schematically in the Figure. This reaction scheme requires that at low nitric acidity the bulk nitrous acid component is molecular HNO_2 , but that with increasing nitric acid progressive dehydration makes N_2O_3 the bulk component above *ca.* 25 moles %. At higher concentrations it is known that the bulk component of nitrous acid is N_2O_4 , and that in pure nitric acid it is ionised to give nitrosonium ions (which probably exist as NO^+NO_2^-). Therefore at higher nitric acid concentrations exchange should occur by such reactions as :



Unfortunately decomposition of nitrous acid occurs so rapidly in nitric acid above *ca.* 32 moles % that quantitative measurements of exchange rate could not be made in this region, although qualitatively it appeared that the exchange was not instantaneous. Above this region exchange between nitric acid and water occurs in the absence of nitrous acid (Part I).

The suggested reaction scheme implies that in nitrosations in aqueous acidic media, involving the nitrosonium ion, NO^+ , this ion is derived from the neutral molecules N_2O_3 , or N_2O_4 , rather than by dehydration of the nitrous acidium ion, H_2NO_2^+ . In this respect

the situation is not analogous to nitration, where the nitronium ion, NO_2^+ , is derived from H_2NO_3^+ . In nitration where the bulk reactivity of the aromatic compound is high compared to that of water, zero-order kinetics are observed (Hughes, Ingold, and Reed, *J.*, 1950, 2400), but in nitrosations where NO^+ is derived from N_2O_3 observation of zero-order kinetics will require the organic compound to be more reactive than the highly nucleophilic nitrite ion, and such a compound would probably react directly with N_2O_3 , itself a strong nitrosating agent (Hughes, Ingold, and Ridd, *Nature*, 1950, 166, 642).

It is not easy to correlate the evidence of isotopic exchange with that from other sources, particularly under the experimental conditions used. However, independent evidence for the postulated reactions (a) is provided by the kinetic study of diazotisation in aqueous acidic media (Hughes, Ingold, and Ridd, *loc. cit.*); and ionisations of N_2O_3 and N_2O_4 , reactions (b) and (c), have been discussed by Hughes, Ingold, and Reed (*loc. cit.*) in their consideration of the nitrous acid anticatalysis of aromatic nitration. Also spectroscopic and conductometric measurements in 100% nitric acid show that N_2O_4 is completely ionised under these conditions (Goulden and Millen, *J.*, 1950, 2620).

EXPERIMENTAL

Materials.—Nitric acid and isotopically enriched water were prepared and purified by the methods outlined in Part I (*loc. cit.*).

Kinetic Procedure.—Solutions were made up by weight, and the general methods were those outlined in Part I (*loc. cit.*), except that no sulphamic acid was added, and nitrous acid was allowed to develop, or its concentration augmented by the addition of sodium nitrite. The rates of exchange (irrespective of labelling) were calculated from the isotopic data as previously described. Two typical runs are illustrated in Table 2.

TABLE 2. Nitrous-acid-catalysed exchange, at 0°.

Run No. 13. $[\text{HNO}_3] = 8.2$ mole %. Abundance of heavy water (β_0') = 1.76 atoms % excess. Final abundance of nitric acid (α_∞') = 1.392 atoms % excess.

t (hr.)	0	1	2	3	4	5	6
α'	0.091	0.176	0.264	0.337	0.404	0.460	0.522
$\log_{10}(\alpha_\infty' - \alpha')$	0.114	0.085	0.052	0.023	1.995	1.969	1.939
$10^3 [\text{HNO}_2]$ (moles %)	2.99	3.14	2.84	2.99	2.74	2.70	2.44

$$R = 3.75 \times 10^{-4} \text{ mole \% sec.}^{-1}.$$

Run No. 63. $[\text{HNO}_3] = 28.31$ mole %. Abundance of heavy water (β_0') = 1.72 atoms % excess. Final abundance of nitric acid (α_∞') = 0.787 atom % excess.

t (min.)	0	3	6	9
α'	0.240	0.414	0.500	0.582
$\log_{10}(\alpha_\infty' - \alpha')$	1.738	1.572	1.458	1.312
$10^3 [\text{HNO}_2]$ (moles %)	2.16	—	2.25	2.14

$$R = 7.03 \times 10^{-2} \text{ mole \% sec.}^{-1}.$$

Determination of Nitrous Acid.—The lower oxides of nitrogen were determined, during each kinetic run, after dilution in water, as described in Part I. This modification of the Griess-Ilosvay method depends on diazotisation in acid solution and coupling in alkaline solution, and the colour development is independent of time. It is probable that the measurement of nitrous acid at such low concentrations (*ca.* 10^{-3} moles %) is the limiting factor in the accuracy of our kinetic method.

The authors are indebted to Professors E. D. Hughes, F.R.S., and C. K. Ingold, F.R.S., for their continued interest. They are grateful to the Humanitarian Trust and the Friends of the Hebrew University for a maintenance grant to one of them (E. A. H.).