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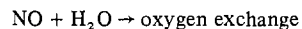
## Simultaneous Nitrogen and Oxygen Exchange ( $\text{NO-H}_2\text{O}$ and $\text{NO-NO}_2^-$ ) between Nitric Oxide and Aqueous Solutions of Nitrite<sup>1</sup>

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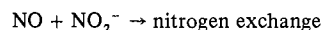
Received August 23, 1972

Kinetic experiments have been carried out in exploration of the simultaneous exchange reactions  $^{15}\text{NO-NO}_2^-$  (nitrogen) and  $\text{NO-H}_2^{18}\text{O}$  (oxygen). N exchange occurs without simultaneous O exchange in solutions of nitrite at high pH to which no free acid is added. This exchange depends upon  $\text{HNO}_2$ , however, and may be quenched by increasing the concentration of  $\text{OH}^-$ . N exchange is faster than O exchange in acid solution at very low concentrations of  $\text{HNO}_2$ , but the two exchange rates become equal for  $[\text{NO}_2^-] = 0.016 M$  in the vicinity of  $[\text{HNO}_2] = 2 \times 10^{-3} M$ , and O exchange then becomes faster at higher nitrous acid concentrations. At fixed  $[\text{HNO}_2]$  concentrations the rate of O exchange decreases with increasing  $[\text{NO}_2^-]$ , but N exchange appears to be zero order in  $[\text{NO}_2^-]$  in acid solution. Temperature coefficient measurements show that a single N-exchange process is operative in acid and alkaline solutions; activation energies of  $17.1 \pm 1.2$  and  $7.0 \pm 0.7$  kcal mol<sup>-1</sup> have been measured for O- and N-exchange processes, respectively. The rate law for N exchange is found to be  $R = k[\text{NO}][\text{HNO}_2]$ , thus implying a transition state or intermediate species  $\text{HN}_2\text{O}_3$ . The rate law for O exchange, deduced somewhat more speculatively than in the case of N exchange, appears most plausibly to be  $R = k[\text{NO}][\text{H}^+][\text{HNO}_2]$ . It is postulated that oxygen exchange is limited by an  $\text{H}_2\text{O-NO}_2^-$  exchange in which NO is a direct, catalytic participant which attacks  $\text{H}_2\text{NO}_2^+$  with possible formation of an intermediate species  $\text{N}_2\text{O}_2^+$ .

In a previous communication<sup>2</sup> it was reported that nitric oxide does not exchange oxygen atoms with pure water but that exchange will take place in dilute aqueous solutions of nitrous acid. It was further reported that the simultaneous processes



and



occur at different rates. These observations were based upon measurements of changes in the isotope ratios 33/31 and 31/30 in a  $^{15}\text{N}$ -enriched NO gas phase brought into intimate contact with a solution of nitrous acid and nitrite ion in  $^{18}\text{O}$ -enriched water. In this paper the results of further kinetic studies of these atom-exchange processes are described.

### Experimental Section

**1. Reaction Cell and Phase Mixing.** The experiments reported in this paper were conducted in exchange-reaction cells substantially different from those described in ref 2. In order to maintain equilibrium between dissolved and gaseous NO with the highest possible efficiency, so that phase mixing cannot impose a rate limitation, magnetic stirring devices have been replaced by a mechanical vibrator ("Vibro-Mixer," manufactured by A. G. für Chemie-Apparaturbau, Zurich).<sup>3</sup> The cell (Figure 1) is affixed to the vibrator through a glass rod sealed to its bottom surface and is attached to a vacuum line through about eight turns of a glass coil, sufficient to absorb the mechanical shock developed by the vibrator. Temperature control is achieved by rapid circulation of water through an outer envelope on the cell, which is deliberately made thin to prevent damping of the vibration and consequent loss of phase-mixing efficiency. The vibrator mounting rod is attached to the inner wall of the cell, rather than to the outer envelope. Under design conditions developed for our experiments, the vibration causes droplets to separate from the entire surface of the liquid layer, maintaining a continuous fountain of solution "mist" in intimate contact with the gas phase. We are satisfied that phase mixing has not been a rate-limiting factor in the rate data reported in this paper.

**2. Kinetic Experiments.** In these experiments  $^{15}\text{NO}$  is held in intimate contact with a solution of potassium nitrite and nitrous acid in  $\text{H}_2^{18}\text{O}$ , and gas samples are withdrawn at measured time intervals for isotopic analysis. In preparation for a typical experiment, potassium nitrite solution in  $\text{H}_2^{18}\text{O}$  is first outgassed in the reaction cell by repeated freeze-pump-thaw cycles. A small quantity of  $\text{HClO}_4$  solu-

tion, held in the separate "finger" vessel which communicates with the cell through a stopcock (see Figure 1), is similarly outgassed. Immediately before initiation of a kinetic run, the  $\text{HClO}_4$  solution is introduced into the cell by rotation of this vessel with the stopcock in open position. This stopcock is then closed and  $^{15}\text{NO}$  is admitted to the cell at a pressure in the vicinity of 150 Torr. Zero time corresponds to the instant of introduction of NO to the cell, and vibration is initiated as close to that instant as possible. NO samples are withdrawn from the gas phase by opening the three-way stopcock momentarily to the sample volume (Figure 1); a momentary interruption of vibration is necessary as each sample is withdrawn. Each sample is passed through a helical trap held at Dry Ice temperature to remove water vapor and then condensed at liquid nitrogen temperature in a sample storage bulb. After kinetic run samples have been taken, NO and solution are held in contact until isotopic equilibrium is achieved, and additional gas samples are then taken for determination of the needed equilibrium isotope ratios.

Performance of kinetic runs as described above requires transfer of NO samples to storage bulbs and pumping of the sample volume between sample withdrawals. These operations impose a limitation to the rate of reaction that can be investigated: 2 min is approximately the lower limit of exchange half-life that can be measured by this method. Some improvement in this aspect was achieved by modification of the cell to include four sample volume enclosures permitting intermediate sample storage. This modification lowered the limit of measurement feasibility to include exchange half-lives of approximately 10 sec. Exchange plots of high quality have been obtained in experiments employing this modified reaction cell.

For conditions in which  $[\text{NO}_2^-]$  is substantially in excess of the concentration of  $\text{HClO}_4$  added, we assume that  $[\text{HNO}_2]$  is fixed by the latter. Perchlorate ion is taken to be an inert species with respect to the processes involved, and as such was also used for maintenance of constant ionic strength in certain experiments to be described below.

$\text{HClO}_4$  and  $\text{NO}_2^-$  solutions were outgassed separately and brought together at the latest possible instant in order to avoid loss of  $\text{HNO}_2$  by disproportionation to NO and  $\text{NO}_3^-$ . Since the rate law for this process is<sup>4</sup>

$$-\frac{d[\text{HNO}_2]}{dt} = k \frac{[\text{HNO}_2]^4}{P_{\text{NO}}^2}$$

there is an apparent possibility of almost instantaneous loss of  $\text{HNO}_2$  during the interval immediately preceding admission of NO. This possibility was checked by performing kinetic experiments with and without NO pressure in the cell in advance of  $\text{HClO}_4$  introduction, but under otherwise identical conditions. Concordant results were obtained, indicating negligible loss of  $\text{HNO}_2$  by disproportionation before introduction of NO. This suggests that the law given above cannot be valid in the region of extremely low NO pressures. The

(1) Research supported by the National Science Foundation, Grant No. GP-6469.

(2) F. T. Bonner, *Inorg. Chem.*, **9**, 190 (1970).

(3) As described by K. Bar-Eli and F. S. Klein, *J. Chem. Soc.*, 1378 (1962).

(4) E. Abel and H. Schmidt, *Z. Phys. Chem., Stoichiom. Verwandtschaftslehre*, **132**, 55 (1928); **134**, 279 (1928).

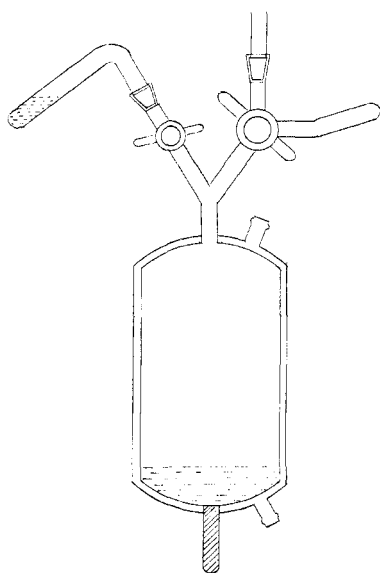


Figure 1. Reaction cell.

possibility of appreciable disproportionation of  $\text{HNO}_2$ , occurring during the time required to complete a kinetic run is considered in a later section.

**3. Isotopic Analysis.** All exchange-rate data are based upon direct mass spectrometry of nitric oxide. The instrument employed is a CEC 21-130, single-collector, cycloidal-focusing mass spectrometer operated on-line to an IBM 1800 computer system. Mass spectrometer output is cabled directly to the computer, where it is recorded digitally on a magnetic disk in the form of 2000 data points per sweep recorded at constant intervals. Thirty-two sweeps of the mass range 30–33 are normally recorded. A change of gain ( $\times 128$ ) is routinely required between 31 and 33 to take into account the very much smaller size of the latter peak. Following appropriate averaging of the data, they are then numerically processed for determination of the ratios of peak areas to provide the desired isotope ratios 33/31 and 31/30. Statistical analysis indicates that a precision of  $\pm 0.5\%$  was achieved for measurements of the generally larger ratio 31/30, and  $\pm 1\%$  for 33/31, which has values extending as low as 0.002 at natural abundance.

**4. Materials.**  $^{15}\text{NO}$  was made by treating  $\text{Na}^{15}\text{NO}_2$  with iodide ion in acid solution, employing nitrite enriched to about 30% in  $^{15}\text{N}$ . Following a repeated sequence of distillation and passage through a helical trap held at the melting temperature of *sec*-butyl chloride, the purity of the gas was high, as evaluated by mass spectrometry. The  $\text{NO}$  gas was stored at pressures considerably below 1 atm.

$\text{H}_2$   $^{18}\text{O}$  initially at about 1.6 atom % enrichment, and normalized in deuterium content, was employed; labeled water was reclaimed by triple distillation for use in later experiments (as isotopically diluted by previous use).

Reagent grade  $\text{HClO}_4$  and  $\text{KNO}_2$  were used without further purification; the concentrations reported are based upon analyses of stock solutions employed in preparing experimental systems.

**5. Decomposition of  $\text{HNO}_2$ .** It was necessary to establish whether  $\text{HNO}_2$  disproportionation could cause a significant change in the composition of an exchange system during the interval of time required to measure an exchange rate. Using the rate constant given by Abel and Schmidt<sup>4</sup> for  $\text{HNO}_2$  disproportionation at  $25^\circ$ , only negligible losses are predicted for  $P_{\text{NO}} = 200$  Torr and  $[\text{HNO}_2] = 10^{-3} M$ , but the decomposition may amount to as much as 6% of initial concentration after 100 min if  $[\text{HNO}_2] = 10^{-2} M$ . Because of the importance of this point, an optical cell was constructed in which it was possible to outgas nitrite solutions and admit  $\text{HClO}_4$  and  $\text{NO}$  gas under experimental conditions identical with those used in our kinetic runs. By ultraviolet spectrophotometry, using the absorption characteristic of  $\text{HNO}_2$  at 353 nm, the rate of disappearance of  $\text{HNO}_2$  from solution could then be followed. The method was found to be capable of detecting changes of 0.2% in  $[\text{HNO}_2]$ . For  $[\text{HNO}_2]_0 = 0.004 M$  and  $P_{\text{NO}} = 200$  Torr, no decomposition could be detected after 240 min; for  $[\text{HNO}_2] = 0.01 M$  the concentration was 98.5% of its initial value after 60 min and 96% after 210 min (*i.e.*, substantially slower decomposition than predicted by the Abel and Schmidt rate law); for  $[\text{HNO}_2]_0 = 0.03 M$ , the  $\text{HNO}_2$  concentration had diminished to 91% of the initial value after 10 min and to 71% after 60 min. In the latter case,  $[\text{HNO}_2]$  is somewhat greater than the

highest  $\text{HNO}_2$  concentration used in our kinetic experiments, and since the exchange experiments in this region are generally completed within 10 min or less, we conclude that under all experimental conditions employed, no appreciable  $\text{HNO}_2$  decomposition could occur within the time necessary to obtain rate measurements.

**6. Treatment of Data.** For atomic exchange between components *a* and *b* in a system of constant chemical composition, the McKay rate law is

$$-\frac{d \ln(1-f)}{dt} = \frac{a+b}{ab} R$$

where *R* represents the net rate of atom transfer between components, *f* is the fraction exchanged at time *t*, and *a* and *b* are the concentrations of *a* and *b*. The experimental quantities  $f_{\text{O}}$  and  $f_{\text{N}}$  for oxygen and nitrogen exchange in this study are given by the expression

$$f = \frac{x_t - x_0}{x_\infty - x_0}$$

where for O exchange

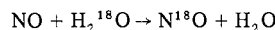
$$x = \frac{33}{33 + 31}$$

and for N exchange

$$x = \frac{30}{30 + 31}$$

Isotope effects are neglected in the above rate expression, since isotope fractionation at equilibrium amounts to only about 2.5% in both cases.<sup>5</sup>

For the case of the overall exchange



it is necessary to take into account all of the oxygen atoms present in the exchange pool, *i.e.*, those in  $\text{H}_2\text{O}$ , in both gaseous and dissolved  $\text{NO}$ , in  $\text{NO}_2^-$ , and in  $\text{HNO}_2$ . If all species in solution except dissolved  $\text{NO}$  are at equilibrium on a time scale rapid with respect to the overall rate of exchange, the quantities *a* and *b* in the McKay law will be  $a = [\text{NO}]$  and  $b = \{[\text{H}_2\text{O}] + 2[\text{NO}_2^-]_0\}$ . Here the "concentration" term  $[\text{NO}]$ , for the heterogeneous systems employed here, is the total number of moles of  $\text{NO}$  present in gas and solution phases divided by the volume of the aqueous phase. The quantity  $[\text{NO}_2^-]_0$  is the initial concentration of nitrite present before acidification, *i.e.*,  $[\text{NO}_2^-]_0 = [\text{NO}_2^-] + [\text{HNO}_2]$ , and the factor of 2 is necessary to express moles of oxygen atoms present in this form. In this instance, since  $\{[\text{H}_2\text{O}] + 2[\text{NO}_2^-]_0\} \gg [\text{NO}]$ , the exchange rate law becomes simplified to

$$-\frac{d \ln(1-f_{\text{O}})}{dt} = \frac{R_{\text{O}}}{[\text{NO}]}$$

If the overall oxygen exchange is rate limited by the rate of  $\text{H}_2\text{O}$ - $\text{NO}_2^-$  exchange, however,  $a = [\text{H}_2\text{O}]$ , and  $b = \{[\text{NO}] + 2[\text{NO}_2^-]_0\}$ . Over the range of conditions employed in this study the quantity  $(a+b)/ab$  differs from  $1/b$  by less than 1%, so the rate law for the  $\text{H}_2\text{O}$ - $\text{NO}_2^-$  limiting case is taken to be

$$-\frac{d \ln(1-f_{\text{O}})}{dt} = \frac{R_{\text{O}}}{[\text{NO}] + 2[\text{NO}_2^-]_0} = R_{\text{O}}'$$

Values of  $R_{\text{O}}$  presented in subsequent sections of this paper have been calculated on the basis of the above rate law. In practice we have obtained values of the slopes  $R_{\text{O}}'$  of exchange plots, which are accurately linear in virtually all instances (see Figure 2), and calculated  $R_{\text{O}}$  by multiplication by the quantity  $\{[\text{NO}] + 2[\text{NO}_2^-]_0\}$ . An ambiguity is introduced, however, by the fact that the  $\text{NO}$  content of each system is reduced at intervals during a kinetic run by sampling. We assume the exchange process to be kinetically first order with respect to  $[\text{NO}]$ , as will be discussed, and therefore  $R_{\text{O}}$  decreases with each sample withdrawal to an extent proportional to  $[\text{NO}]$ . The decrease in  $R_{\text{O}}$  is compensated in part by decrease in the denominator, to an extent that decreases with increasing nitrite concentration. In the typical case the total stepwise decrease in  $[\text{NO}]$  is 10% or less, and the ambiguity introduced by this method of

(5) (a) S. Jordan and F. T. Bonner, *J. Chem. Phys.*, **54**, 4963 (1971); (b) L. L. Brown and J. S. Drury, *ibid.*, **48**, 1400 (1968).

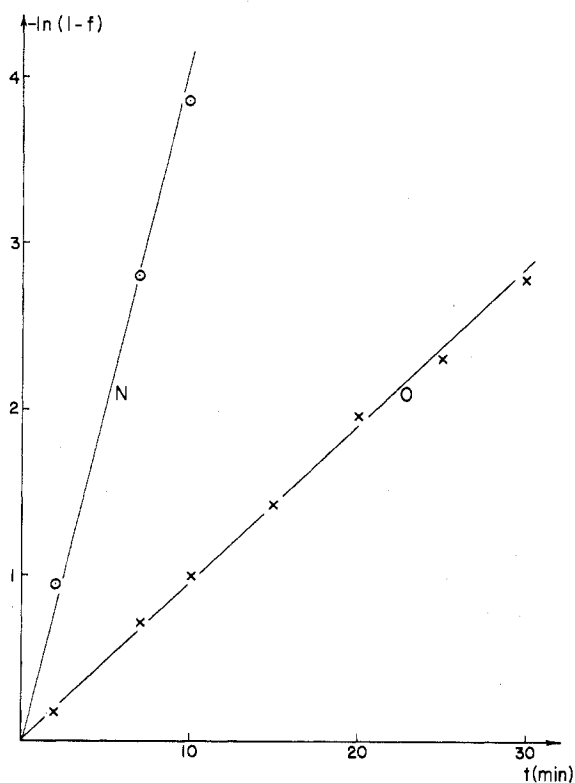
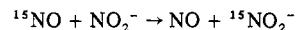


Figure 2. Typical exchange plot where  $[\text{NO}_2^-] = 0.0157 \text{ M}$  and  $[\text{HNO}_2] = 0.005 \text{ M}$ :  $\times$ , oxygen;  $\circ$ , nitrogen.

obtaining  $R_O$  values is generally small. It is in any event less than in the case of the alternative method of plotting  $\{[\text{NO}] + 2[\text{NO}_2^-]_0\} \ln(1-f_O)$  vs.  $t$ . The value of  $[\text{NO}]$  used in the concentration term is based upon the average value of  $P_{\text{NO}}$  over the interval pertaining in each measurement.

In the case of nitrogen atom exchange



$a = [\text{NO}]$  and  $b = [\text{NO}_2^-]_0$ , where again  $[\text{NO}]$  is total nitric oxide divided by solution volume, and  $[\text{NO}_2^-]_0$  is the sum of nitrite ion and nitrous acid concentrations. As in the case of oxygen exchange, we have measured the slopes  $R_N'$  of exchange plots (see Figure 2) and then calculated

$$R_N = R_N' \frac{[\text{NO}][\text{NO}_2^-]_0}{[\text{NO}] + [\text{NO}_2^-]_0}$$

basing  $[\text{NO}]$  on the average value of  $P_{\text{NO}}$  in each measurement. If N exchange is also first order with respect to  $[\text{NO}]$  (see below), sample withdrawal produces a stepwise decrease in  $R_N$  which is partially compensated by an increase in

$$\frac{[\text{NO}] + [\text{NO}_2^-]_0}{[\text{NO}][\text{NO}_2^-]_0}$$

the extent of the latter increasing with  $[\text{NO}_2^-]$  and providing nearly exact compensation at the higher levels of nitrite concentration employed here. As in the case of oxygen, the ambiguity associated with this effect does not appear to be substantial, and the method employed is preferable to the alternative of plotting

$$\frac{[\text{NO}][\text{NO}_2^-]_0}{[\text{NO}] + [\text{NO}_2^-]_0} \ln(1-f_N) \text{ vs. } t$$

There is an additional consequence of stepwise NO removal that must be considered, *i.e.*, the change in isotopic composition brought about by sampling. While this is completely negligible in the case of O exchange, in which the total  $^{18}\text{O}$  content of the system is effectively fixed by the large molar quantity of  $\text{H}_2\text{O}$ , it is appreciable in the case of N-exchange since the total  $^{15}\text{N}$  content of the system is determined by the relatively small number of moles of NO introduced. Withdrawal of NO at intervals before isotopic equilibrium is reached therefore has the effect of changing the quantity  $x_\infty$ . Throughout each individual kinetic run there is thus a step-function shift in this

equilibrium quantity, and for the correct determination of the quantity  $f_N$  it is in principle necessary to calculate a new value of  $x_\infty$  for each point. This has been done numerically for the standard case in which the sample volume is about 2% of total gas volume, and the difference between the slope  $R_N'$  as determined in this way and as determined by using an experimentally measured value of  $x_\infty$  is found to be negligible for up to eight points. Withdrawal of a large NO sample gives a nonnegligible effect, however, that must be taken into account.

The quantities  $R_O$  and  $R_N$ , obtained as described above, are not intrinsic rates but depend upon the experimental configuration employed, because of the presence of an extended reservoir of NO gas in equilibrium with the aqueous solution phase in which exchange occurs. Correction of rate  $R$  to a value  $R_0$  intrinsic to the aqueous layer alone can be accomplished, for processes that are first order in NO, by use of the relationship

$$R_0 = R \frac{\text{total moles of NO}}{\text{moles of dissolved NO}}$$

For this purpose we have used the values for NO solubility in water given by Winkler.<sup>6</sup> While this has been done only in the necessary case of our temperature dependence measurements, any  $25^\circ$  value of  $R$  can be converted to  $R_0$  for the configuration used in this study (total volume 150 ml, solution volume 10.0 ml) by multiplying by the constant factor  $3.00 \times 10^2$ .

**7. Error Limits—Reproducibility.** The precision of individual isotope ratio measurements was in the range 0.5–1.0% as previously indicated. There was in general very little tendency toward scatter on the part of points on individual exchange plots (see Figure 2). Error analysis based on these factors leads to the conclusion that the error limits in exchange rates generally lie between 5 and 10% of the values reported. Precision of these values as judged from the results of replicate experiments was not always so satisfactory, however; reproducibility ranged from a few per cent to, on occasion, 10–20%. Small uncertainties in final equilibrium isotope ratios can contribute substantial error in those instances in which exchange is far advanced before the first sample is withdrawn. Minor uncertainties in chemical composition, such as would be brought about by incomplete transfer of  $\text{HClO}_4$  solutions through the stopcock, may be a contributing factor in the occasional instances of poor reproducibility. Surface effects may also play a part in these instances, since the vibrator produces a fine mist of droplets and keeps the reaction cell walls bathed in solution at all times.

## Results

**1. Nitrogen Exchange in Solutions of High pH.** The occurrence of  $\text{NO}-\text{NO}_2^-$  nitrogen exchange and  $\text{NO}-\text{H}_2\text{O}$  oxygen exchange at different rates suggested the possibility of a direct attack of NO upon  $\text{NO}_2^-$ . If so, there should be observable N exchange, but no O exchange, in solutions of  $\text{NO}_2^-$  prepared without addition of free acid. This postulate was tested by conducting exchange experiments in  $\text{KNO}_2$  solutions to which no  $\text{HClO}_4$  was added to form  $\text{HNO}_2$ . As shown in Table I, slow exchange of nitrogen between NO and  $\text{NO}_2^-$  was observed over the concentration range  $[\text{NO}_2^-] = 0.0157\text{--}1.780 \text{ M}$ , corresponding to a pH range of about 7.8–8.8. This finding contradicts a report cited by Brown and Drury<sup>5b</sup> that NO and  $\text{NO}_2^-$  do not exchange nitrogen atoms in the absence of added free acid. Two of the experiments reported in Table I, at  $[\text{NO}_2^-] = 0.0157$  and  $0.890 \text{ M}$ , were conducted in  $^{18}\text{O}$ -labeled  $\text{H}_2\text{O}$  solution. While appreciable nitrogen exchange was observed in both cases, no oxygen exchange could be detected during contact periods as long as 4 days (*i.e.*, initial and final values of 33/31 were identical within an experimental error of less than 2%). These observations are consistent with a hypothesis of direct attack of NO upon  $\text{NO}_2^-$ , if one assumes that NO diatomic units are exchanged in this process but that oxygen exchange between  $\text{NO}_2^-$  and solvent  $\text{H}_2\text{O}$  requires an appreciable concentration of  $\text{HNO}_2$ . It would appear that even direct  $\text{NO}-\text{NO}_2^-$  exchange is dependent upon  $\text{HNO}_2$ , how-

**Table I.** N Exchange between NO and NO<sub>2</sub><sup>-</sup> in Solutions of High pH at 24.5°

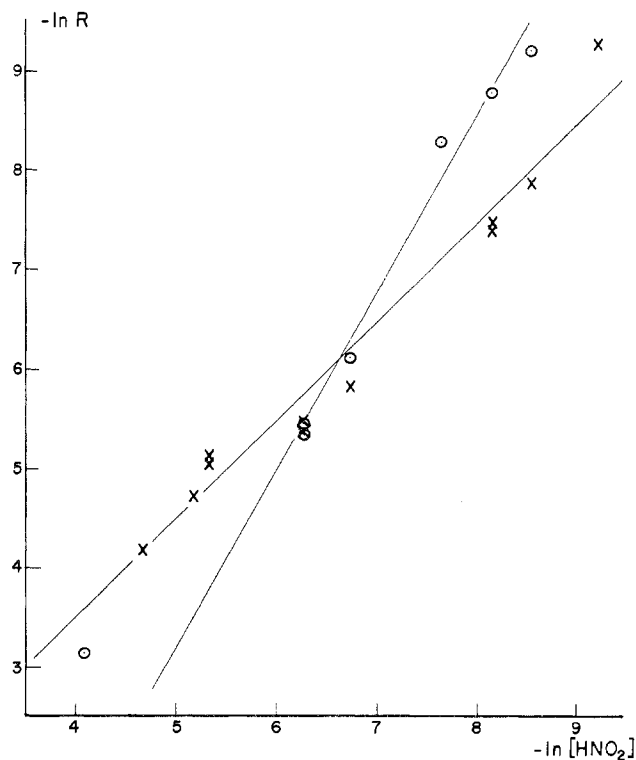
[NO <sub>2</sub> <sup>-</sup> ], M	10 <sup>5</sup> R <sub>N</sub> , M min <sup>-1</sup>	[NO <sub>2</sub> <sup>-</sup> ], M	10 <sup>5</sup> R <sub>N</sub> , M min <sup>-1</sup>
0.0157	0.125	0.472	2.34
0.0460	0.230	0.890	4.16
0.090	0.974	1.78	4.84
0.181	1.85		

ever, because of the following observation: for a solution made 0.110 M in KOH and 0.890 M in KNO<sub>2</sub> and a second one made 0.528 M in KOH and 0.472 M in KNO<sub>2</sub>, no nitrogen exchange could be detected during 7 hr of contact, although substantial exchange took place during the same period in solutions at the same NO<sub>2</sub><sup>-</sup> concentrations but without added OH<sup>-</sup> (see Table I). These experiments, carried out in an attempt to obtain a series of alkaline solution rate measurements at constant ionic strength, indicate that the small concentrations of HNO<sub>2</sub> produced by hydrolysis in these solutions are essential to the N exchange observed. The same small concentration of HNO<sub>2</sub> is evidently insufficient to produce detectable O exchange between NO<sub>2</sub><sup>-</sup> and H<sub>2</sub>O in the extended time periods employed.

In the series of experiments reported in Table I the degree of completion of exchange ranges from about 5% at the lower concentrations to 25% at [NO<sub>2</sub><sup>-</sup>] = 0.890 M. In cases of small exchange fraction the experimental error in rate is considerably larger than our general estimate of 5–10% and may be as high as 25% at the lower concentrations. The exchange rates reported in Table I do reveal a clear trend toward increasing exchange rate with increasing [NO<sub>2</sub><sup>-</sup>], however, despite the presence of substantial errors of measurement. There may also be an uncertainty introduced by the variation of ionic strength over a considerable range, and there is an unevaluated possibility that NO solubility may vary somewhat with nitrite concentration. A least-squares treatment of the data yields a value of 0.81 for the apparent kinetic order of exchange with respect to [NO<sub>2</sub><sup>-</sup>], with an uncertainty of at least ±0.3. If a transition state or intermediate species HN<sub>2</sub>O<sub>3</sub> were involved, *i.e.*, for a rate law  $R_N = k[\text{NO}] \cdot [\text{HNO}_2]$ , the kinetic order with respect to NO<sub>2</sub><sup>-</sup> would be 0.5, since the concentration of hydrolysis-produced HNO<sub>2</sub> varies with the square root of [NO<sub>2</sub><sup>-</sup>]. This possibility appears to be reasonably encompassed, but not proven, within the limitations of these data.

**2. Dependence of Exchange Rates on [HNO<sub>2</sub>] in Acid Solution.** Results of kinetic experiments performed to evaluate the dependence of O- and N-exchange rates on [HNO<sub>2</sub>] are shown graphically in Figure 3. Most of these measurements were carried out at a fixed initial concentration [NO<sub>2</sub><sup>-</sup>] = 0.0157 M, and the oxygen-exchange rates have been corrected to that value as an equilibrium concentration, on the basis of the observed nitrite dependence described in the next section. Since this correction is probably not valid over substantial concentration intervals, only those data for which this correction is small have been shown. No correction has been applied to nitrogen-exchange rates, since this process appears to be independent of nitrite ion concentration in acid solutions (see below). The range of HNO<sub>2</sub> concentration employed in these measurements is 10<sup>-4</sup>–10<sup>-2</sup> M.

As shown in Figure 3, O exchange is slower than N exchange at the lower concentrations, but appears to be more steeply dependent upon [HNO<sub>2</sub>] in this region at least, so that the rates come together at about the midpoint of the range. At the concentration 0.0019 M, for example, our measurements of  $R_N$  and  $R_O$  yield the identical value 0.0047 mol l.<sup>-1</sup> min<sup>-1</sup>. The line drawn through the oxygen-exchange points does not

**Figure 3.** Dependence of exchange rates on [HNO<sub>2</sub>] at [NO<sub>2</sub><sup>-</sup>] = 0.0157 M, 24.5°: ○, O exchange; ×, N exchange.

take the one high concentration value (0.017 M) into account. This point reflects a higher exchange rate than predicted by the trend for nitrogen exchange but lower than that based upon the apparent trend for oxygen at lower concentrations. Several additional measured values for  $R_O$ , not shown because of the need for large corrections for nitrite concentration, also fall generally in the region between the two lines shown in Figure 3. While it is our impression that the crossover in exchange rates is real, the differences between N- and O-exchange rates in this region are not large, and our data are not abundant.

A least-squares treatment of the oxygen-exchange points excluding the high concentration value yields a value of 1.76 for the slope of the line shown in Figure 3. Including that point, the least-squares value becomes 1.45.

Using all the points shown for nitrogen exchange in Figure 3, the least-squares slope of the line drawn for that process is 0.997, strongly implying that N exchange is kinetically first order with respect to HNO<sub>2</sub>. In Figure 4, the N-exchange rate dependence has been replotted on a scale compressed so that the alkaline solution rate data obtained at [NO<sub>2</sub><sup>-</sup>] = 0.0157 and 0.046 M can be included. For these points, hydrolysis concentrations of HNO<sub>2</sub> were calculated using the value  $4.6 \times 10^{-4}$  for  $K_a$ . As is seen in the drawing, these points fit well with the acid solution data on a line of very nearly unit slope, implying an essential continuity in the N-exchange processes observed in acid and in alkaline solutions. As has been stated, no oxygen-exchange process could be detected under these conditions.

**3. Dependence of Exchange Rates on [NO<sub>2</sub><sup>-</sup>].** Experiments were conducted at varying concentrations of nitrite ion (0.0044–0.181 M) and at two separate concentrations of HNO<sub>2</sub> (0.0003 and 0.0012 M). The results of these measurements are shown graphically in Figure 5. It is clear that the oxygen-exchange rate decreases with increasing [NO<sub>2</sub><sup>-</sup>] at both [HNO<sub>2</sub>] levels employed. Nitrogen exchange, on the other hand, displays no more than a slight opposite trend,

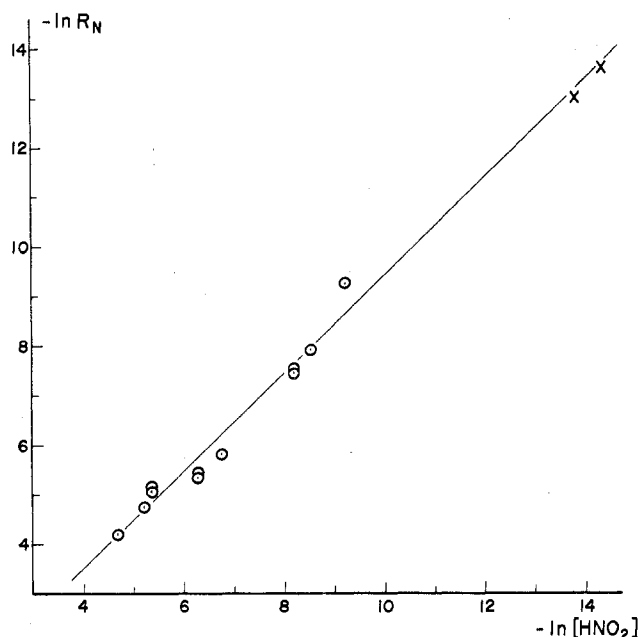


Figure 4. Dependence of nitrogen exchange rate on  $[\text{HNO}_2]$  at  $[\text{NO}_2^-] = 0.0157 \text{ M}$ ,  $24.5^\circ$ :  $\circ$ , acid solution data;  $\times$ , alkaline solution data.

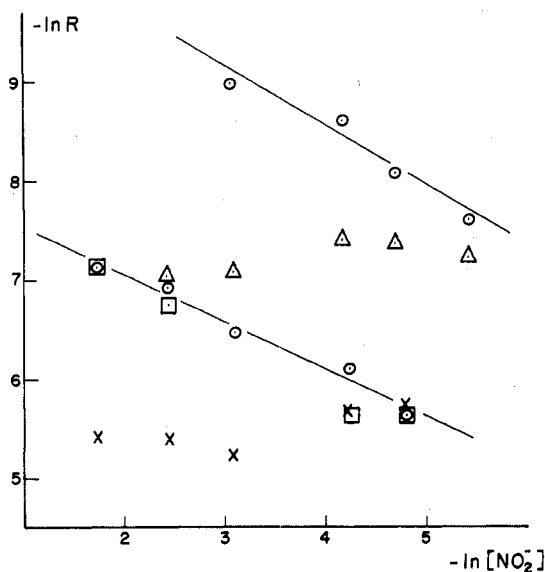


Figure 5. Dependence of exchange rates on  $[\text{NO}_2^-]$  at  $24.5^\circ$  and two fixed concentrations of  $[\text{HNO}_2]$ :  $\circ$ , O exchange, upper curve at  $[\text{HNO}_2] = 0.0003 \text{ M}$ , lower curve at  $[\text{HNO}_2] = 0.0012 \text{ M}$ ;  $\Delta$ , N exchange at  $[\text{HNO}_2] = 0.0003 \text{ M}$ ;  $\times$ , N exchange at  $[\text{HNO}_2] = 0.0012 \text{ M}$ ;  $\square$ , O exchange at  $[\text{HNO}_2] = 0.0012 \text{ M}$  and constant ionic strength 0.181.

and we conclude that  $R_N$  is independent of  $[\text{NO}_2^-]$  within the range of conditions employed in these experiments.

In the case of the  $[\text{HNO}_2]$ -dependence measurements described in the last section, very little variation of ionic strength was involved. Since the measurements reported in Figure 5 were carried out over a substantial range of ionic strength, however, several additional rate measurements were made at  $[\text{HNO}_2] = 0.0012 \text{ M}$  and an ionic strength rendered constant at 0.181 by the addition of  $\text{NaClO}_4$ . The results of these measurements are in reasonable accord with the data obtained without added perchlorate in both nitrogen- and oxygen-exchange cases; only oxygen-exchange points at constant ionic strength are designated in Figure 5. Independence of ionic strength indicates that a neutral molecular species is

involved, consistent with our supposition of first-order kinetic dependence of both exchange processes upon  $[\text{NO}]$ .

The inverse dependence of  $R_O$  upon  $[\text{NO}_2^-]$  appears to be steeper at the lower of the two  $\text{HNO}_2$  concentrations. The least-squares slopes of the two lines shown in Figure 5 are  $-0.59$  at  $0.0003 \text{ M}$  and  $-0.48$  at  $0.0012 \text{ M}$ , with an estimated error of  $\pm 0.04$  in each case.

**4. Temperature Coefficients of Exchange Rates.** Results of exchange rate measurements carried out over the temperature range  $10\text{--}40^\circ$  are summarized in Table II and in Figure 6. To make meaningful rate comparisons at different temperatures it is of course essential to take the solubility of  $\text{NO}$  into account, so that the quantities that are tabulated are values of  $R_O$  as defined previously. For this purpose, values of  $\text{NO}$  solubility were taken from ref 6. Temperature-dependence measurements were also carried out for  $\text{N}$  exchange in  $0.890 \text{ M}$  nitrite solutions at high pH (no acid added); the slope of this plot is in good agreement with the slope of the plotted acid solution measurements as shown. Activation energies calculated from the Arrhenius plots for the two exchange processes are as follows: O exchange,  $17.1 \pm 1.2 \text{ kcal/mol}$ ; N exchange (acid solution),  $7.1 \pm 0.6 \text{ kcal/mol}$ ; N exchange (alkaline solution),  $6.9 \pm 0.8 \text{ kcal/mol}$ .

#### Discussion

Oxygen exchange has been studied previously under exceedingly dilute conditions,<sup>2</sup> such that the exchange rate law approaches very closely to the simple form

$$\frac{d \ln(1-f)}{dt} = \frac{R_O}{[\text{NO}]}$$

(see, e.g., Figure 1 in ref 2). Under these conditions the acquisition of rigorously linear exchange plots over a sizable number of  $\text{NO}$  samples is a convincing demonstration that O exchange is first order in  $[\text{NO}]$ , a conclusion that is reinforced by the observation that linearity is unaffected by deliberate withdrawal of very large gas samples. While the situation seems more complicated in the case of more concentrated systems as employed in this study, we are confident that the conclusion drawn from dilute systems is valid over the entire range of concentrations involved. In the case of  $\text{N}$  exchange the rate law precludes straightforward demonstration on this point, but our general experience with nitrogen-exchange plots, and in particular with experiments carried out at relatively high nitrite concentration in which very large gas samples have been deliberately withdrawn, leads us to the strong supposition that this process is also kinetically first order with respect to  $[\text{NO}]$ .

It is clear from the different temperature coefficients and activation energies that separate  $\text{N}$ - and  $\text{O}$ -exchange mechanisms are operative in this system. The consonance of temperature coefficients for acid and alkaline solution measurements indicates that a single mechanism is responsible for nitrogen exchange over the entire range of conditions investigated. The evidence that the process is first order with respect to  $[\text{HNO}_2]$  and zero order with respect to  $[\text{NO}_2^-]$  in acid solution appears unambiguous, and if our assumption concerning the dependence upon  $[\text{NO}]$  is correct, the rate law for this process has the form  $R_N = k[\text{NO}][\text{HNO}_2]$ . We therefore presume that the process occurs *via* a transition state or intermediate of composition  $\text{HN}_2\text{O}_3$ . A species of this composition capable of leading to nitrogen exchange would most probably be bound between nitrogen atoms, and exchange would then involve an intramolecular oxygen rearrangement and subsequent  $\text{N-N}$  bond cleavage. The process of nitrogen atom exchange between  $\text{NO}$  and  $\text{NO}_2^-$  will there-

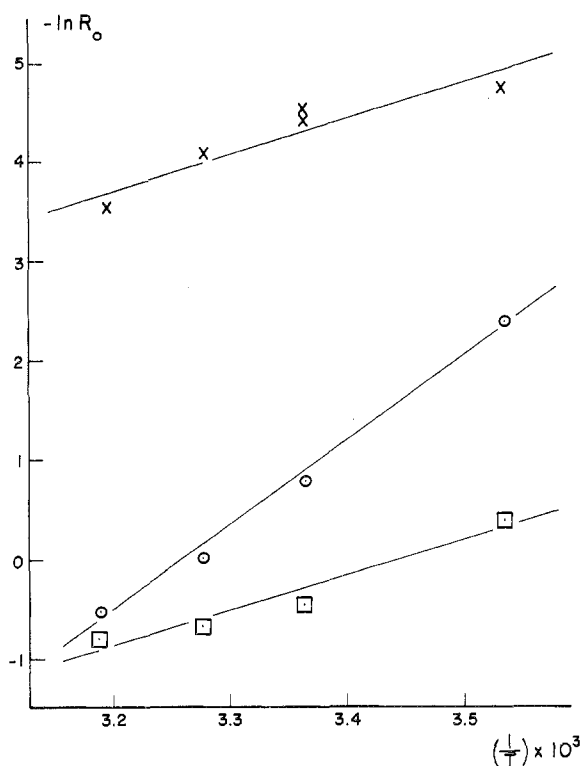


Figure 6. Temperature coefficients of exchange processes:  $\square$ , N exchange,  $[\text{NO}_2^-] = 0.0452 \text{ M}$ ,  $[\text{HNO}_2] = 0.0012 \text{ M}$ ;  $\times$ , N exchange,  $[\text{NO}_2^-] = 0.890 \text{ M}$ , no  $\text{H}^+$  added;  $\circ$ , O exchange,  $[\text{NO}_2^-] = 0.0452 \text{ M}$ ,  $[\text{HNO}_2] = 0.0012 \text{ M}$ .

Table II. Temperature Coefficient Measurements

Temp, $^{\circ}\text{C}$	$R_{\text{N}}'$ , $\text{min}^{-1}$	$R_{\text{O}}'$ , $\text{min}^{-1}$	$(R_{\text{N}})_{\text{O}}$ , $\text{M min}^{-1}$	$(R_{\text{O}})_{\text{O}}$ , $\text{M min}^{-1}$
$[\text{NO}_2^-] = 0.0452 \text{ M}$ , $[\text{HNO}_2] = 0.0012 \text{ M}$				
9.9	0.086	0.0018	0.693	0.0923
24.5	0.155	0.0071	1.59	0.470
32.0	0.149	0.0153	2.00	1.03
40.5	0.193	0.0234	2.32	1.72
$[\text{NO}_2^-] = 0.890 \text{ M}$ , No $\text{H}^+$ Added				
10.0	0.00035		0.0081	
24.5	0.00041		0.012	
24.5	0.00038		0.011	
32.0	0.00051		0.017	
40.0	0.00092		0.029	

fore be expected to carry oxygen atoms to the gas phase at isotopic composition representative of the solution nitrite as exchange proceeds.

The conclusion expressed in ref 2, that N exchange was everywhere faster than O exchange under the conditions of that study, was based upon an incomplete interpretation of the data. As shown in this paper, which encompasses the range of conditions employed in ref 2, nitrogen exchange is faster than oxygen exchange in the region of low acidity, but the rates become equal and appear to cross over, O exchange becoming faster than N exchange with increasing  $\text{HNO}_2$  concentration. While the interpretation of N-exchange data seems to be straightforward despite this complexity, interpretation of O exchange is rendered difficult and uncertain. Our evidence is unfortunately not sufficient to support a definitive elucidation of the oxygen-exchange mechanism, and we emphasize in advance that much of the following discussion is necessarily speculative in character.

Oxygen exchange is complicated by the circumstance that a multicomponent-exchange system is involved. Use of the

McKay rate law is valid only if there is a single rate-limiting step, and the two alternative possibilities of  $\text{NO}-(\text{H}_2\text{O}-\text{NO}_2^-)$  or  $\text{H}_2\text{O}-(\text{NO} + \text{NO}_2^-)$  rate limitation lead to the alternative exchange rate laws previously described. Values of  $R_{\text{O}}$  differ from one another only in that the quantity  $R_{\text{O}}'$  is multiplied by  $[\text{NO}]$  in the first case and by  $\{[\text{NO}] + 2[\text{NO}_2^-]_{\text{O}}\}$  in the second. Thus rates calculated on the first assumption will be somewhat smaller than those calculated on the second assumption, but there is little information in the different calculated rates that can assist in identifying the more correct of the two, if any. The negative slopes of the oxygen-exchange lines in Figure 5 are somewhat steeper than shown if it is the quantity  $R_{\text{O}}'[\text{NO}]$  that is plotted, but the slopes of O-exchange lines in Figures 3 and 6 are very little affected.

As the  $\text{HNO}_2$  concentration is increased (Figure 3) and the two exchange rates come together and cross over, it is expected that the N-exchange process may make some contribution to O exchange, and it is probably doubtful that any single step can be identified as rate determining. If so, the use of the McKay law may be of questionable validity, but our data are not sufficient in either numbers or precision to warrant complex exchange-reaction analysis. We therefore seek to deal with the extreme of a process that can be assumed separable and note that the slope of the O-exchange line in Figure 3 approaches 2. We postulate a process that is second order in  $\text{HNO}_2$ . We note that the O-exchange rate decreases with increasing  $[\text{NO}_2^-]$  at fixed  $[\text{HNO}_2]$  (Figure 5) and that the negative slope may increase with decreasing  $[\text{HNO}_2]$ . We postulate a process that is  $-1$  order in  $\text{NO}_2^-$ . Putting these postulates together with our prior conclusion that O-exchange is first order in  $\text{NO}$ , we obtain the rate law

$$R_{\text{O}} = k[\text{NO}][\text{HNO}_2]^2/[\text{NO}_2^-] = k'[\text{NO}][\text{H}^+][\text{HNO}_2]$$

While the above rate law is speculative, we believe it to be plausible and reasonably reflective of the trends and indications our data provide. In particular, the demonstration of distinct activation energies and the existence of marked inverse dependence of  $R_{\text{O}}$  on  $[\text{NO}_2^-]$  although  $R_{\text{N}}$  is independent of  $[\text{NO}_2^-]$  would appear to rule out the possibility that  $^{18}\text{O}$  transfer to the gas phase is simply controlled by the N-exchange process after the two rates have come together.

As stated previously, we have chosen to present our oxygen-exchange data on the basis of an assumed  $\text{H}_2\text{O}-\text{NO}_2^-$  rate limitation, and this exchange process in the absence of  $\text{NO}$  is one that has been extensively studied previously. Anbar and Taube<sup>7</sup> found the rate law for  $\text{NO}_2^- - \text{H}_2\text{O}$  exchange, in phosphate-buffered systems and in the same pH range involved here, to be  $R = k[\text{H}^+]^2[\text{NO}_2^-]$ , indicating hydrated nitrosium ion,  $\text{H}_2\text{NO}_2^+$ , as the activated complex. Bunton, *et al.*,<sup>8,9</sup> found  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange to proceed according to the second-order rate law  $R = k[\text{HNO}_2]^2$  in unbuffered solutions at high nitrite concentrations, but according to the rate law  $R = k[\text{H}^+][\text{HNO}_2][\text{OAc}^-]$  in the presence of acetate buffer, indicating catalysis by the acetate anion. The uncatalyzed process is interpreted as proceeding *via*  $\text{N}_2\text{O}_3$  as the intermediate. Bunton and Stedman<sup>10</sup> have reported a rate law for  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange identical with that of Anbar and Taube in solutions of low nitrite concentration ( $<0.05 \text{ M}$ ) and have suggested a divergence of kinetic path-

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(9) C. A. Bunton and M. Masui, *J. Chem. Soc.*, 304 (1960).

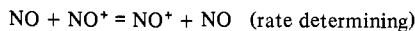
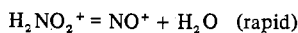
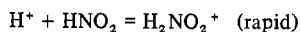
(10) C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 3466 (1959).

ways with the species  $\text{H}_2\text{NO}_2^+$  responsible for exchange at low nitrite and  $\text{N}_2\text{O}_3$  the favored intermediate in the region of higher nitrite.

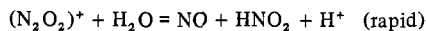
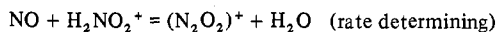
Because of differences in the conditions employed, only rough comparisons may be made between our values of oxygen-exchange rates and  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange rates reported in the literature. Such comparisons seem to indicate that our rates  $(R_{\text{O}})_0$  are consistently higher. *E.g.*, for Anbar and Taube<sup>7</sup> experiment 1.52 ( $[\text{NO}_2^-] = 0.01 \text{ M}$ ,  $[\text{NaClO}_4] = 0.99 \text{ M}$ , pH 4.43), the reported oxygen-exchange rate is  $R = 3.3 \times 10^{-3} \text{ M min}^{-1}$ ; for our experiment 99 ( $[\text{NO}_2^-] = 0.0083 \text{ M}$ ,  $[\text{NaClO}_4] = 0.173 \text{ M}$ ,  $[\text{NO}] = 0.1 \text{ M}$ , pH 4.20),  $(R_{\text{O}})_0 = 1.08 \text{ M min}^{-1}$ . For Anbar and Taube<sup>7</sup> experiment 1.06 ( $[\text{NO}_2^-] = 0.25 \text{ M}$ ,  $[\text{OAc}^-] = 0.1 \text{ M}$ , pH 5.70),  $R = 5 \times 10^{-4} \text{ M min}^{-1}$ ; for our experiment 42 ( $[\text{NO}_2^-] = 0.18 \text{ M}$ ,  $[\text{NO}] = 0.1 \text{ M}$ , pH 5.5),  $(R_{\text{O}})_0 = 0.24 \text{ M min}^{-1}$ . Converting the three values in Table III of ref 10 from 0 to 25° on the assumption that our measured oxygen-exchange activation energy is applicable, we obtain rate values that are smaller than our own  $(R_{\text{O}})_0$  values under comparable conditions by factors of 420, 17, and 24, respectively. (Two of the rates reported in ref 10, incidentally, show an increase in O-exchange rate with increasing  $[\text{NO}_2^-]$  at fixed  $[\text{HNO}_2]$ . This is contrary to our observation of a depression of rate with increasing  $[\text{NO}_2^-]$  and seems also inconsistent with the rate law conclusions subsequently drawn in ref 10.)

The question whether  $\text{H}_2\text{O}-\text{NO}_2^-$  is or is not rate limiting in the extreme of a separable O-exchange process is essentially a question of whether NO plays a catalytic role in that process, if our rate law is correct. Our rate expression is analogous to that reported by Bunton and Masui<sup>9</sup> for  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange catalyzed by acetate ion, with the latter species here replaced by NO. If  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange is not rate limiting, then the overall rate of  $\text{NO}-\text{H}_2\text{O}$  exchange is controlled by interaction of NO with a species whose concen-

tration is fixed by  $\text{H}_2\text{NO}_2^+$ ; *i.e.*, our rate law could be explained by the sequence



If  $\text{H}_2\text{O}-\text{NO}_2^-$  is rate limiting, however, our rate law implies a direct catalytic attack of NO upon the hydrated nitrosonium ion itself



The comparisons of our rate data with literature values for  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange indicate a striking catalytic activity on the part of NO, an indication that is hardly diminished if the comparison is based upon rates calculated without assuming an  $\text{NO}_2^-$ - $\text{H}_2\text{O}$  rate limitation. It would be difficult to rationalize these comparisons on the basis of an assumption other than an  $\text{H}_2\text{O}-\text{NO}_2^-$  process that is catalyzed by NO. We therefore postulate an oxygen-exchange process whose rate is limited by  $\text{H}_2\text{O}-\text{NO}_2^-$  exchange but in which NO is a participating species. We again emphasize the necessarily speculative nature of our several conclusions about the oxygen-exchange mechanism; we are also unable to assess the possibility of a competing  $\text{N}_2\text{O}_3$ -exchange pathway at increased nitrite concentrations, as suggested by Bunton, *et al.*<sup>8,10</sup>

**Registry No.** NO, 10102-43-9;  $\text{H}_2\text{O}$ , 7732-18-5;  $\text{HNO}_2$ , 7782-77-6;  $\text{NO}_2^-$ , 14797-65-0;  $\text{N}_2$ , 7727-37-9;  $\text{O}_2$ , 7782-44-7.

**Acknowledgments.** The authors are grateful to Mrs. Janine Menes for technical assistance, to Dr. Yoshi Okaya for assistance in developing the mass spectrometer-computer interface and associated programming, and to Dr. Norman Sutin for helpful discussions.

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## Nitrogen and Oxygen Exchange between Nitric Oxide and Aqueous Solutions of Nitric Acid<sup>1</sup>

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Received August 23, 1972

The simultaneous processes  $\text{NO} + \text{H}_2\text{O} \rightarrow \text{O}$  exchange and  $\text{NO} + \text{NO}_3^- \rightarrow \text{N}$  exchange have been explored by isotopic analysis of  $^{15}\text{NO}$  brought into contact with aqueous solutions of  $\text{HNO}_3$  in  $\text{H}_2^{18}\text{O}$ . Exchange has been observed in the concentration range 0.05–0.94  $\text{M HNO}_3$  but only after a characteristic induction time which at each concentration is longer for N exchange than for O exchange. The induction period is related to production of  $\text{HNO}_2$  by oxidation of NO by  $\text{HNO}_3$ . Linear exchange plots are obtained for systems at chemical equilibrium, and O exchange is found to be much faster than N exchange under all conditions explored. Neither atom exchange occurs between NO and  $\text{NO}_3^-$  in neutral solution. Nitrogen exchange has been shown to be limited by  $\text{NO}_3^-$ - $\text{HNO}_2$  exchange, at an overall rate that appears to correspond to the reversible  $\text{NO}-\text{HNO}_2$  reaction under equilibrium conditions. This same process will produce oxygen exchange, but  $\text{NO}-\text{H}_2\text{O}$  oxygen exchange has been found to occur at a much greater rate, in a process that is assumed to proceed *via*  $\text{HNO}_2$  without involvement of nitrate, probably by a mechanism similar to that pertaining in all-nitrite systems.

In this paper we report the results of an investigation of simultaneous nitrogen and oxygen atom exchange between NO gas and aqueous nitric acid solutions, in extension of previously reported studies of exchange processes between

NO and solutions of nitrite.<sup>2</sup> In this study the rate of oxygen exchange has been found greater than that of nitrogen exchange under all conditions employed. Also, in the case of nitric acid, we find characteristic induction periods at

(1) Research supported by the National Science Foundation, Grant No. GP-6469.

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