ways with the species $H_2NO_2^+$ responsible for exchange at low nitrite and N_2O_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 H_2O-NO_2^- exchange rates reported in the literature. Such comparisons seem to indicate that our rates $(R_O)_0$ are consistently higher. *E.g.*, for Anbar and Taube[7] experiment 1.52 ($[NO_2^-] = 0.01\,M$, $[NaClO_4] = 0.99\,M$, pH 4.43), the reported oxygen-exchange rate is $R = 3.3 \times 10^{-3}\,M\,\text{min}^{-1}$; for our experiment 99 ($[NO_2^-] = 0.0083\,M$, $[NaClO_4] = 0.173\,M$, $[NO] = 0.1\,M$, pH 4.20), $(R_O)_0 = 1.08\,M\,\text{min}^{-1}$. For Anbar and Taube[7] experiment 1.06 ($[NO_2^-] = 0.25\,M$, $[OAc^-] = 0.1\,M$, pH 5.70), $R = 5 \times 10^{-4}\,M\,\text{min}^{-1}$; for our experiment 42 ($[NO_2^-] = 0.18\,M$, $[NO] = 0.1\,M$, pH 5.5), $(R_O)_0 = 0.24\,M\,\text{min}^{-1}$. 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 $(R_O)_0$ 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 $[NO_2^-]$ at fixed $[HNO_2]$. This is contrary to our observation of a depression of rate with increasing $[NO_2^-]$ and seems also inconsistent with the rate law conclusions subsequently drawn in ref 10.)

The question whether H_2O-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[9] for H_2O-NO_2^- exchange catalyzed by acetate ion, with the latter species here replaced by NO. If H_2O-NO_2^- exchange is not rate limiting, then the overall rate of NO-H_2O exchange is controlled by interaction of NO with a species whose concentration is fixed by $H_2NO_2^+$; *i.e.*, our rate law could be explained by the sequence

$$H^+ + HNO_2 = H_2NO_2^+ \quad \text{(rapid)}$$
$$H_2NO_2^+ = NO^+ + H_2O \quad \text{(rapid)}$$
$$NO + NO^+ = NO^+ + NO \quad \text{(rate determining)}$$

If H_2O-NO_2^- is rate limiting, however, our rate law implies a direct catalytic attack of NO upon the hydrated nitrosonium ion itself

$$NO + H_2NO_2^+ = (N_2O_2)^+ + H_2O \quad \text{(rate determining)}$$
$$(N_2O_2)^+ + H_2O = NO + HNO_2 + H^+ \quad \text{(rapid)}$$

The comparisons of our rate data with literature values for H_2O-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 NO_2^--H_2O rate limitation. It would be difficult to rationalize these comparisons on the basis of an assumption other than an H_2O-NO_2^- process that is catalyzed by NO. We therefore postulate an oxygen-exchange process whose rate is limited by H_2O-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 N_2O_3-exchange pathway at increased nitrite concentrations, as suggested by Bunton, *et al.*[8,10]

Registry No. NO, 10102-43-9; H_2O, 7732-18-5; HNO_2, 7782-77-6; NO_2^-, 14797-65-0; N_2, 7727-37-9; O_2, 7782-44-7.

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Nitrogen and Oxygen Exchange between Nitric Oxide and Aqueous Solutions of Nitric Acid[1]

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The simultaneous processes $NO + H_2O \rightarrow O$ exchange and $NO + NO_3^- \rightarrow N$ exchange have been explored by isotopic analysis of ^{15}NO brought into contact with aqueous solutions of HNO_3 in $H_2{}^{18}O$. Exchange has been observed in the concentration range 0.05–0.94 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 HNO_2 by oxidation of NO by 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 NO_3^- in neutral solution. Nitrogen exchange has been shown to be limited by NO_3^--HNO_2 exchange, at an overall rate that appears to correspond to the reversible NO-HNO_3 reaction under equilibrium conditions. This same process will produce oxygen exchange, but NO-H_2O oxygen exchange has been found to occur at a much greater rate, in a process that is assumed to proceed *via* 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.[2] 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

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[1] Research supported by the National Science Foundation, Grant No. GP-6469.

[2] (a) F. T. Bonner, *Inorg. Chem.*, 9, 190 (1970); (b) F. T. Bonner and S. Jordan, *ibid.*, 12, 1363 (1973).

each HNO_3 concentration for which exchange was observed, the induction period for oxygen exchange being smaller than that for nitrogen exchange in each instance.

There have been several literature reports concerning nitrogen exchange between NO and NO_3^-,[3-5] NO_2^- and NO_3^-,[6] and NO and NO_2^-.[7] In addition, oxygen exchange between NO and H_2O in concentrated nitric acid solutions is well known.[8-10] For the most part, these studies have been concerned with isotope fractionation rather than the kinetic and mechanistic aspects of the exchange processes involved. Winter, *et al.*,[11] showed that water does not exchange oxygen atoms with nitrate ion in neutral solution but obtained complete exchange at 100° in 1 *N* H_2SO_4. Hall and Alexander[12] demonstrated that exchange does not occur in basic solution and reported no detectable H_2O-NO_3^- exchange for nitrate in 0.2 *M* HNO_3. Klein and Friedel[13] observed oxygen exchange between water and 40% solution of nitric acid. Bunton, *et al.*,[14-16] have studied the kinetics of oxygen exchange between H_2O and HNO_3 in solutions in the concentration range 8-66 mol % HNO_3 and observed exchange in the lower end of this range (8-28 mol %) only in the presence of HNO_2. The results reported here, involving the presence of an NO gas phase, have been obtained for systems in the concentration range 0.05-1 *M* HNO_3. These are dilute relative to the systems studied by Bunton, *et al.*, but necessarily more concentrated than the 0.0024 *M* solution for which no oxygen exchange could be detected as previously reported in ref 2a.

Experimental Section

Aqueous solutions of nitric acid in $H_2{}^{18}O$ were brought into intimate contact with ^{15}NO gas by vibration of a reaction cell, and exchange of both nitrogen and oxygen was followed by sampling of the gas phase at intervals for mass spectrometric analysis, all as described elsewhere.[2b] Experiments involving relatively fast kinetics were carried out in the modified cell described in ref 2b, which permits gas sampling from the reaction vessel at 10-sec intervals. The labeled H_2O employed contained ^{18}O in the range 1-1.5 atom %. ^{15}NO was prepared at about 30% enrichment by reaction of $Na^{15}NO_2$ with iodide in acid solution, followed by rigorous purification. Reagent grade nitric acid was used without further purification. Where needed in several experiments as described below, ^{15}N-enriched HNO_3 was employed (initially 95% ^{15}N).

When NO is brought in contact with HNO_3 solution, the system is subject to the well-known, reversible reaction

$$2NO + H^+ + NO_3^- + H_2O = 3HNO_2$$

and nitrous acid must be accounted as among the species present. Because all of our experiments involved HNO_3 concentrations below 1 *M*, we assume the gas phase consisted exclusively of NO and H_2O and that the liquid phase was limited to the principal species H^+, NO_3^-, NO, HNO_2, NO_2^-, and H_2O. In order to determine HNO_2 concentrations quantitatively, an optical cell was constructed in which conditions identical with those pertaining in our kinetic experiments could be established. HNO_2 concentrations in reacting and equilibrium NO-HNO_3 systems were then measured by uv absorption, following established procedures for simultaneous nitrate-nitrite analysis.[17] These were based principally upon the HNO_2 absorption maximum at 386 nm, and a Cary 14 spectrophotometer was employed. The limit of error of these concentration measurements is estimated to be about 5%.

Results and Discussion

(a) General Behavior. As reported in ref 2a, no O exchange between NO and H_2O is detectable after 3 hr of contact at $[HNO_3] = 0.0024\,M$, yet it is known that exchange is rapid in concentrated HNO_3. Accordingly, a "threshold" nitric acid concentration for both N and O exchange was sought. At $[HNO_3] = 0.094\,M$ and a temperature of 24.5°, the first signs of oxygen exchange (but not nitrogen exchange) became detectable after 240 min of contact between the phases. At higher concentrations, smaller induction periods were observed, the period for oxygen exchange being always smaller than that for nitrogen exchange. At $[HNO_3] = 0.318\,M$, for example, the induction period for N exchange was found to be 50 min, but O exchange was made evident by an increasing 33/31 ratio after about 30 min in the same experiment.

Characteristically, a raw-data plot of the logarithmic exchange functions $-\ln(1 - f_O)$ and $-\ln(1 - f_N)$ against time, where f_O and f_N represent the fractions of oxygen and nitrogen atoms exchanged, shows first the two induction periods followed by two separate exchange curves. Each exchange curve exhibits curvature in its early stages, and each is in turn followed by a linear region, the linear region being achieved earlier for oxygen than for nitrogen exchange. Also characteristically, the slope of the linear portion of the O-exchange curve is greater than that of the N-exchange curve at a given initial concentration of HNO_3. Finally, while the slopes of the linear portions of N-exchange curves vary with HNO_3 concentration, the corresponding slopes for O exchange were observed to have closely similar values over a substantial range of HNO_3 concentrations (0.32-1.0 *M*).

Since NO-H_2O exchange[2a] and NO_3^--H_2O exchange at "low" HNO_3 concentration[14] are known to depend upon HNO_2, we associate the induction periods for both exchanges with the time required for a critical minimum concentration of the latter species to be produced by reaction between NO and HNO_3. The rate laws for reaction between NO and HNO_3 in the presence of HNO_2 and for the opposing process of HNO_2 disproportionation have been shown[18,19] to be

$$+\frac{d[HNO_2]}{dt} = k_1[HNO_2][H^+][NO_3^-]$$

and

$$-\frac{d[HNO_2]}{dt} = k_2\frac{[HNO_2]^4}{P_{NO}{}^2}$$

where k_1 and k_2 have the values 1.6 and 46, respectively, at 25°, with concentrations in moles per liter, pressure in atmospheres, and time in minutes. The autocatalytic property of the forward reaction is consistent with our observation of relatively long induction time followed by rapid increase in the rate of exchange if HNO_2 is the responsible species.

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Since in a true isotopic exchange process a linear exchange plot implies constancy of chemical composition, it was necessary to establish whether the attainment of linearity in our exchange curves corresponded to the achievement of chemical equilibrium among the species involved. Figure 1 shows the results of three separate experiments bearing on this point for the case of nitrogen exchange. Curve 1 shows the spectrophotometrically measured increase in $[HNO_2]$ with time for a given quantity of NO in intimate contact with 10 ml of HNO_3 solution at an initial concentration of 0.46 *M*. Curve 2 is the N-exchange curve observed under identical conditions, and as seen, the HNO_2 concentration levels off toward a constant value as the linear portion of this curve begins. The final HNO_2 concentration observed in this and similar experiments corresponds closely to values calculated from the reported equilibrium constant value of 28.7 at 25°.[19] Curve 3 in Figure 1 shows the results of an experiment in which NO was preequilibrated chemically with HNO_3 solution, and the system was then isotopically disequilibrated by addition of a small quantity of $H^{15}NO_3$ solution, the overall conditions corresponding nearly identically with those pertaining in curves 1 and 2. For this experiment the concentration of HNO_2 has effectively its equilibrium value at $t = 0$, and the exchange plot obtained by sampling of the NO gas phase as the system approaches isotopic equilibrium is accordingly linear along the entire period of observation. The fact that this plot is parallel to the linear portion of curve 2 shows identical nitrogen-exchange rates in the two experiments and demonstrates that the latter corresponds closely to an equilibrium system. Most of the N-exchange rate measurements reported in a later section were obtained by carrying out experiments similar to that represented by curve 2. The reversible NO–HNO_3 reaction itself would be expected to produce nitrogen exchange, and the question therefore arises as to whether the rate of this reaction at equilibrium is identical with the exchange process observed, as will be discussed in the next section.

Figure 2 shows a set of experiments on O exchange similar to those shown for N exchange in Figure 1, but at a lower concentration of HNO_3. Curve 1 shows the rate of increase of HNO_2 concentration with time, and curve 2 the corresponding exchange plot. As can be seen, the exchange plot attains an apparently linear region while $[HNO_2]$ is still undergoing rapid change. The latter part of the exchange curve is therefore not a true exchange plot and cannot be used to provide an O-exchange rate. This conclusion is confirmed by the results of the isotopic disequilibration experiment represented in curve 3 of Figure 2. Here NO and 0.32 *M* HNO_3 were brought to chemical equilibrium, a small quantity of $H_2{}^{18}O$ was then added, and NO samples were removed at intervals for isotopic analysis. As is evident, the actual O-exchange rate under these conditions is very much greater than would be deduced from the steepest part of curve 2. Only experiments conducted by the isotopic disequilibration technique, therefore, can be used for measurement of O-exchange rates. At the concentration shown in Figure 2, the rate was on the edge of measurability by the sampling techniques employed. The similarity of slopes of the linear portions of the O-exchange curves in the concentration range 0.32–1.0 *M* HNO_3 apparently results from a fortuitous combination of rates and nonequilibrium concentrations.

For similar initial partial pressures of NO, the induction periods for both exchanges are observed to decrease with increasing HNO_3 concentration. Induction times in both cases are found to increase with increasing NO pressure. For example, two experiments were carried out at $[HNO_3] = 0.633$ *M*, one at an initial NO partial pressure of 144 Torr and the other at $(P_{NO})_i = 226$ Torr; the induction period observed for N exchange was 15 min at the lower pressure and 20 min at the higher pressure, although the slopes of the linear exchange plots ultimately attained were closely similar (see Figure 3); the corresponding induction times for O exchange in these same experiments were 10 and 15 min.

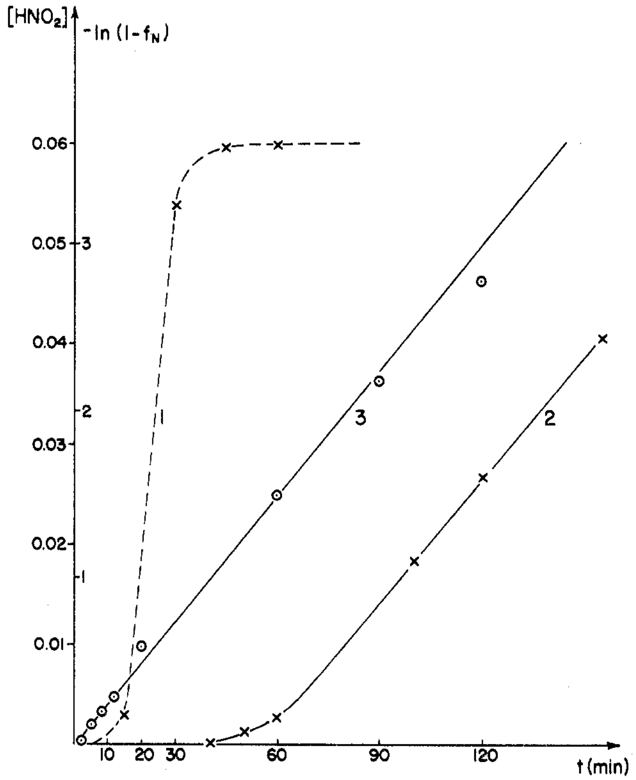

Figure 1. N exchange and $[HNO_2]$ increase for 140 ml of NO (initial pressure 154 Torr) in contact with 10 ml of 0.46 *M* HNO_3 solution at 24.5°.

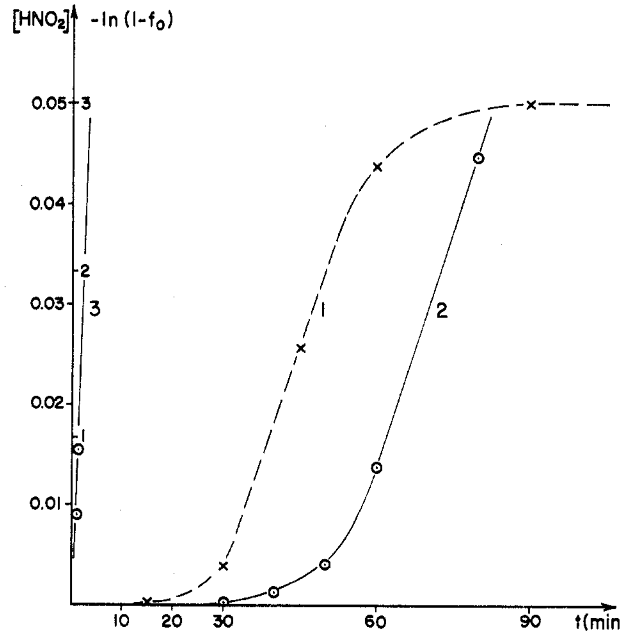

Figure 2. O exchange and $[HNO_2]$ increase for 142 ml of NO (initial pressure 159 Torr) in contact with 10 ml of 0.32 *M* HNO_3 at 24.5°.

To establish whether there might be any exchange processes occurring between NO and nitrate in the absence of HNO_2,

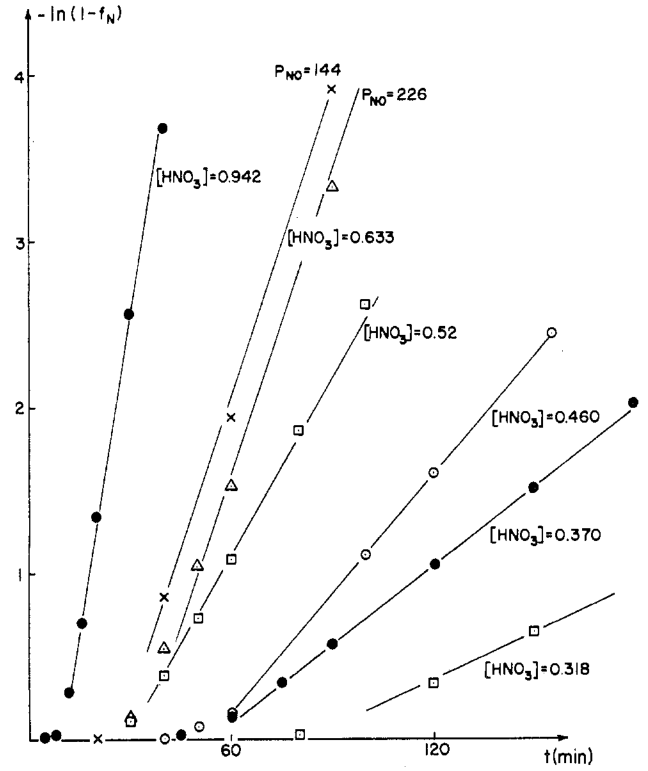

Figure 3. N-exchange curves at various initial concentrations of nitric acid.

an experiment was carried out in which ^{15}NO was held in intimate contact with a 0.3 M solution of KNO_3 in $H_2{}^{18}O$. No exchange of either oxygen or nitrogen was detectable after 2 days.

(b) Nitrogen Exchange. Nitrogen-exchange curves determined in the range of initial HNO_3 concentrations 0.318–0.942 M are shown in Figure 3, and data concerning these and several additional experiments are given in Table I. Equilibrium nitric acid concentrations $[HNO_3]_e$ were obtained by reducing initial nitric acid concentrations by one-third the equilibrium concentrations of HNO_2. The latter (column 2) are measured values obtained at initial NO partial pressure 157 Torr. The initial NO pressures in these experiments ranged from 144 to 226 Torr. From the equilibrium constant expression it can be shown that the equilibrium HNO_2 concentration should fall within 10% of the measured value over the range 144–197 Torr. Calculated values of exchange rates are not shown in the two cases falling outside of this range, and for a majority of the values shown the given HNO_2 concentration should coincide with its equilibrium value to within the error of measurement. The quantity R_N' (column 4) consists of the slopes of the linear portions of the nitrogen-exchange plots, reported for our experimental configuration in which the gas and liquid phases have volumes of 140 and 10 ml, respectively.

If we assume that nitrogen exchange is limited by the rate of NO-HNO_2 exchange, then using the exchange rate law appropriate for this case

$$-\frac{d\ln(1-f_N)}{dt} = \frac{[NO] + \{[NO_3^-] + [HNO_2]\}}{[NO]\{[NO_3^-] + [HNO_2]\}}R_N$$

we calculate the value $R_N = 7.0 \times 10^{-4}\ M\ min^{-1}$ in the slowest instance, for which $[HNO_2] = 0.05\ M$. But this is some 40 times smaller than would be expected for NO-HNO_2 exchange at the same nitrous acid concentration, on the basis of experience with nitrite systems.[2b] It therefore seems reasonable to assume that nitrogen exchange is limited in this system by the rate of NO_3^--HNO_2 exchange. The exchange rate law appropriate in this case

Table I. Nitrogen-Exchange Rate Data, 24.5°

$[HNO_3]_e$, M	$10^2 \times [HNO_2]_e$, M	$(P_{NO})_i$, Torr	$10^2R_N'$, min^{-1}	10^2R_N, $M\ min^{-1}$	$10^2R_N/[HNO_2] \times [HNO_3]^2$, $M^{-2}\ min^{-1}$
0.914	8.2	166	12.9	1.7	0.25
0.609	7.1	144	6.5	0.66	0.25
0.609		226	5.5		
0.499	6.4	197	3.7	0.40	0.25
0.450	6.1	173	2.0	0.22	0.18
0.440	6.0	154	2.6	0.26	0.22
0.352		208	1.5		
0.308	5.2	173	1.4	0.14	0.28
0.301	5.0	172	0.88	0.083	0.18

$$-\frac{d\ln(1-f_N)}{dt} = \frac{[NO_3^-] + \{[NO] + [HNO_2]\}}{[NO_3^-]\{[NO] + [HNO_2]\}}R_N$$

has therefore been used for calculation of the value of R_N shown in column 5 of Table I. In this calculation, equilibrium values of $[NO_3^-]$ and $[HNO_2]$ have been used, and [NO] is the average "concentration" of that species (total moles of NO in both phases divided by solution volume) over the sampling interval, corrected for the quantity consumed in the production of HNO_2. If our assumption that NO does not participate in a rate-limiting step is correct, the rates as reported should be independent of the ratio of gas and solution volumes; hence no correction for experimental configuration has been made.

The range of concentrations accessible to us in the present study was very narrow, and HNO_3 and HNO_2 concentrations have not been independently varied, so that the interpretive value of the rate data given in Table I is limited. In addition, the necessity for periodic sampling of the gas phase introduces a certain ambiguity in that, as each sample is withdrawn, there is a small decrease in NO pressure, uncompensated if the process is not first order in that species, and also a small consequent perturbation of the equilibrium system. Within these limitations, we note the approximate constancy of the quantity $R_N/[HNO_2][HNO_3]^2$, as shown in column 6 of Table I. This would imply a rate law $R = k[H^+][NO_3^-][HNO_2]$, identical with the rate law of Abel and Schmidt for the reaction between NO and HNO_3. If we calculate the forward rate of this reaction under each set of equilibrium conditions, using the Abel and Schmidt value of 1.6 for the rate constant at 25° and correcting appropriately for the activity of nitric acid, we obtain values of the same order of magnitude as the exchange rates given in Table I but consistently higher, by factors between 3 and 4. While we have no ready explanation for this difference, we believe it most plausible to assume that nitrogen exchange in this system results directly from the NO-HNO_3 reaction, an assumption that is supported by the correlation of exchange regions with the onset of equilibrium (Figure 1), the apparent coincidence of rate laws, and the observed increase of induction period with P_{NO}.

Our hypothesis that the overall rate of NO-nitrate exchange is limited by nitrate-nitrite exchange was tested in an additional experiment whose results are represented in Figure 4. ^{15}NO was brought to chemical and isotopic equilibrium with 8.5 ml of 0.36 M HNO_3, the latter containing sufficient ^{15}N to maintain a high content of the heavy isotope in the gas phase. The solution was then suddenly made 0.1 M in nitrite at natural abundance by addition of KNO_2 solution. Sam-

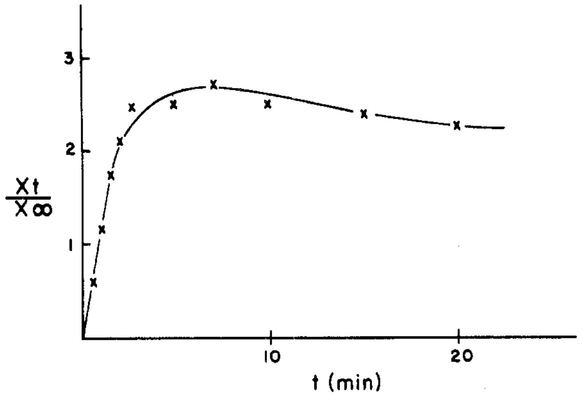

Figure 4. Change in ^{14}N content of the NO gas phase upon addition of $^{14}NO_2^-$ to an equilibrated NO-HNO_3 system containing ^{15}N.

ples of the gas phase were then withdrawn at regular intervals for isotopic analysis. The quantity X_t/X_∞, plotted against time in Figure 4, represents exchange fraction. As seen, the ^{14}N content of the NO gas rises very steeply upon introduction of NO_2^-, attains a maximum value, and then falls gradually toward an equilibrium value. The first part of the curve corresponds to NO-NO_2^- exchange, and the existence of a maximum in the curve shows that this process is very much more rapid than NO_2^--NO_3^- exchange. The gentle decline from the maximum value corresponds to the more leisurely arrival of ^{15}N atoms from nitrate to nitrite, passing from there into the gas phase.

No kinetic investigation of NO_3^--HNO_2 nitrogen exchange has been reported in the literature, but this process in the absence of NO would not be the same as that observed in this study if we are correct in assuming that exchange is controlled by the reversible NO-HNO_3 reaction. The mechanism proposed by Abel, *et al.*, in their interpretation of the rate laws for this reaction, involving reversible processes in which N_2O_4 is formed and interacts with NO in aqueous solution, appears to provide a satisfactory explanation for nitrogen exchange as observed in the present investigation.

(c) **Oxygen Exchange.** As indicated previously, O-exchange rates in these systems were found measurable only by isotopic disequilibration. The results of four such experiments are recorded in Table II. Appropriately long equilibration times were employed (100 hr in the case of 0.05 *M* HNO_3) before the ^{18}O content of solution was slightly altered by adding $H_2{}^{18}O$. Parentheses indicate substantial uncertainty in the value of one HNO_2 concentration because of the low partial pressure of NO employed. The quantity R_O' is the slope of the oxygen-exchange plot, reported for an experimental configuration in which the ratio of gas to liquid phase volume is 14.0.

Table II. Oxygen-Exchange Rate Data, 24.5°

$[HNO_3]_e$, *M*	$[HNO_2]_e$, *M*	$(P_{NO})_i$, Torr	R_O', min^{-1}	$(R_O)_0$, *M* min^{-1}
0.293	0.050	162	0.932	61.2
0.139	(0.032)	105	0.370	13.8
0.089	0.025	158	0.182	8.0
0.044	0.015	177	0.098	4.3

The oxygen-exchange rate observed at initial $[HNO_3]$ = 0.31 *M* is very much greater than nitrogen exchange under similar conditions, and since the process that limits the latter will produce oxygen as well as nitrogen exchange, the process observed here should consist predominantly of NO-H_2O exchange as catalyzed by HNO_2, without involvement of NO_3^-. This conclusion is reinforced by the very low rate of H_2O-HNO_3 exchange observed by Bunton, *et al.*,[16] at their lower limit of HNO_3 concentration (8 mol %); even though our concentrations of HNO_2 are higher, this process is undoubtedly very slow at the low HNO_3 concentration levels involved here. The data of Table II would thus appear to apply to O exchange in nitrite systems extended to a region of low pH and low $[NO_2^-]$ relative to our previous study.[2b] In view of these conclusions, the values $(R_O)_0$ reported in Table II have been calculated on the basis of the rate law

$$-\frac{d\ln(1-f_O)}{dt} = \frac{[H_2O] + \{[NO] + 2[HNO_2]\}}{[H_2O]\{[NO] + 2[HNO_2]\}}R_O$$

simplified to the justifiable approximation

$$R_O = R_O'\{[NO] + 2[HNO_2]\}$$

In this form of the exchange law it is implicit that H_2O-nitrite exchange is rate limiting. We also assume this process to be first order in [NO], as we know it to be under other conditions. We have therefore reported values for the quantity $(R_O)_0$, *i.e.*, rates that would pertain in the absence of a gas phase, by multiplying by the factor $14/RT\beta = 3.00 \times 10^2$ (at 24.5°), where the factor 14 is the ratio of gas to solution volumes, R the gas constant, and β the molar solubility of NO at 1 atm pressure.[2b]

In view of the complexity of this system and the small number of points obtained, there is little basis for speculation concerning the mechanism of oxygen exchange under these conditions. When compared with calculated values for the rate of the NO-HNO_3 reaction at equilibrium under similar conditions, the values $(R_O)_0$ are greater to an extent that increases with decreasing $[HNO_2]$, by factors in the range of 10^4-10^5. The oxygen exchange observed here is occurring by a process quite clearly independent of that reaction. The data of Table II appear to conform approximately to the rate law deduced for oxygen exchange in all nitrite systems,[2b] *i.e.*, $R_O = k[NO][H^+][HNO_2]$, and it seems reasonable to assume that the same mechanism is operative in the two cases. However, while this rate law would predict an increasing exchange rate with decreasing pH, for the one instance in which we can compare values at the same HNO_2 concentration, the present rate is of the same order of magnitude as that observed in an all-nitrite system, despite the fact that the pH was very much higher, and NO_2^- concentration much greater, in the latter instance. This may indicate some alteration of kinetic pathways under the conditions pertaining in this study, possibly including the involvement of species related to NO_3^-. Finally, while we have essentially assumed nonexchange of oxygen between NO and NO_3^- in this treatment, it should be clear that that assumption applies only to the time scale upon which oxygen exchange was observed in these experiments and that such exchange is expected on the more expanded time scale of the NO-HNO_3 reaction and nitrogen atom exchange.

Registry No. NO, 10102-43-9; H_2O, 7732-18-5; HNO_3, 7697-37-2; HNO_2, 7782-77-6; NO_3^-, 14797-55-8; NO_2^-, 14797-65-0; N_2, 7727-37-9; O_2, 7782-44-7.