

In contrast, Yamada's analysis⁸ of the single crystal polarized spectrum of *trans*-[Cr(en)₂Cl₂]Cl·HCl requires a small positive value of κ . His spectral data at room temperature can be fitted reasonably well with $\kappa = +1/3$ and $Dt = -500 \text{ cm}^{-1}$. We then obtain $\delta\sigma \approx -1200 \text{ cm}^{-1}$ and $\delta\pi \approx +1000 \text{ cm}^{-1}$ which imply that the σ and π bondings of the chloride are considerably weaker than those of the fluoride ion. The spectra of the *trans*-dibromo and *trans*-dichloro complexes are similar^{6,10} and the corresponding $\delta\sigma$ and $\delta\pi$ parameters for the bromide ion are not expected to differ very much from the values for the chloride ion. On the other hand the large splitting of the ⁴T_{1g}(a) band in the *trans*-difluoro complex is also found in the *trans*-dihydroxy complex.¹⁰ Thus in the nature of its bonding to a Cr(III) ion the fluoride has little in common with the other halide ions and instead resembles more closely the hydroxide ion. These results are in accord with the recent work of Glerup and Schäffer,¹¹ who reached the same conclusions from a systematic study of the solution spectra of *trans*-[Cr(NH₃)₄X₂] (X = Br⁻, Cl⁻, F⁻, H₂O, OH⁻).

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Oxygen Exchange between Nitric Oxide and Water

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Salts of the anion N₂O₃²⁻ have long been well characterized,² and while free H₂N₂O₃, or " α -oxyhyponitrous acid,"³ has never been isolated, this species and its related anions have been postulated as reaction intermediates in some of the older literature of aqueous solution inorganic nitrogen chemistry. Since NO may be taken to be the stoichiometric anhydride of H₂N₂O₃, aqueous NO solutions have in the past been assumed to contain this species, an assumption which in turn has been employed in mechanistic interpretations.⁴ This view of the status of dissolved NO was bolstered by a

report that aqueous NO solutions exhibit conductivities substantially greater than water,⁵ and its persistence in more recent literature is illustrated by references to the "natural" (acidic) pH of NO solution.⁶ In this study, the nature of aqueous NO has been explored by isotopic exchange, as has been done previously in the case of the apparent anhydride relationship N₂O—H₂N₂O₂.⁷

Experimental Section

NO—H₂O exchange experiments were carried out by vacuum-line techniques, employing a cell designed to give high efficiency of mixing of aqueous and gas phases, adapted from a similar cell employed in H₂—NH₃ exchange studies.⁸ A charge of H₂O¹⁸ was outgassed in a vessel other than the reaction cell by a series of repeated freeze-pump-thaw cycles and then distilled into the reaction cell. After temperature equilibration, ¹⁸NO was then admitted to the cell at measured pressure, and high speed stirring was begun with a motor-driven horseshoe magnet held externally and in line with an internal magnet, the latter sealed in glass and mounted on and at right angles to the vertical mixing shaft in the cell. The gas phase was sampled at intervals by momentarily interrupting the stirring and turning the main (three-way) stopcock to a position providing communication between the cell and a small dead-end sample volume. In a typical cell design the reaction vessel volume was about 100 ml and sample volume was about 2.0 ml; in a typical experiment the partial pressure of NO was between 100 and 200 Torr, and the charge of H₂O was 10.0 ml.

Gas samples were drawn through an extended helical trap held at Dry Ice temperature and then distilled into sample tubes for subsequent mass spectrometric analysis. The possibility of isotope effect in this sampling method was checked by experiment and found to be absent under the conditions employed. The sample volume and purification line were pumped between sampling operations.

For experiments employing a nonvolatile solute (see below), the cell described in ref 8 could not be used. A simpler cell was therefore employed, in which stirring was carried out by a Teflon-enclosed stirring magnet, sealed inside the cell and turned by a motor-driven magnet located below the cell and its associated constant-temperature bath. Adequate outgassing of the Teflon for these experiments required pumping periods up to 12 hr; the Teflon stirring bar was held out of the aqueous phase by an external magnet during this procedure and during outgassing of the solutions employed. While less efficient than the other cell, it was found to provide adequate mixing of phases for kinetic runs of relatively long half-life.

The oxygen-18-enriched H₂O employed in these experiments (Weizmann Institute) was normalized with respect to deuterium and contained 1.667 atom % ¹⁸O (determined by CO₂ equilibration). Nitrogen-15-labeled NO was used in all experiments, and ¹⁵NO at about 34% enrichment was synthesized by vacuum-line techniques, employing the quantitative reaction between NO₂⁻ and I⁻ in acid medium, starting with Na¹⁵NO₂ obtained from the Organization National Industriel de l'Azote, Toulouse. The product NO gas was purified by repeated distillations between liquid *n*-pentane and liquid N₂ and by passage over a molecular sieve material.

Nitrogen-15 enrichment permitted direct mass spectrometry on NO without dependence on mass 32, since exchange of oxygen was detected by measurement of the ratio 33/31 in ¹⁵NO. A single-collector mass spectrometer was employed (Metropolitan-Vickers), and reported ratios are based in each case on average values obtained from ten or more repeated scans. The ratio

(5) E. J. Joss, *ibid.*, **30**, 1270 (1926).

(6) See, e.g., W. A. Seddon and H. C. Sutton, *Trans. Faraday Soc.*, **59**, 2323 (1963).

(7) F. Bonner and J. Bigeleisen, *J. Am. Chem. Soc.*, **74**, 4944 (1952).

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(2) A. Angeli, *Gazz. Chim. Ital.*, **II**, **25**, 17 (1896); **II**, **33**, 245 (1903).

(3) C. C. Addison, G. A. Gamlen, and R. Thomson, *J. Chem. Soc.*, 338 (1952).

(4) See, e.g., M. L. Nichols and C. W. Morse, *J. Phys. Chem.*, **35**, 1238 (1931).

33/31 in this case corresponds to the ratio of molecular concentrations

$$\frac{[^{15}\text{N}^{18}\text{O}] + [^{18}\text{O}^{17}\text{O}]}{[^{16}\text{N}^{18}\text{O}] + [^{14}\text{N}^{17}\text{O}]}$$

While the species $^{16}\text{O}^{17}\text{O}$ can be ignored, the H_2O employed contained about 0.13% ^{17}O , so that a correction for $^{14}\text{N}^{17}\text{O}$ was necessary. At its maximum however, for the case of isotopic equilibrium, the correction amounted to only 0.3%.

Equilibrium values of the ratio 33/31, when needed, were determined experimentally in most cases. For the case of measurements of nitrogen exchange between NO and NO_2^- (see below), equilibrium values of the ratio 31/30 were usually calculated as needed.

Results and Discussion

I. Nonexchange of Oxygen between NO and H_2O in Neutral and Acid Solutions.—It was found that in rigorously pure systems, NO and H_2O do not exchange oxygen atoms at 25°. In one experiment, for example, after 150 hr of contact between NO and liquid H_2O the ratio 33/31 observed in ^{15}NO was 0.00214, contrasted with the value 0.00212 in "standard" ^{15}NO measured at the same time. This difference is within the error of measurement (*ca.* 1%), and nonexchange was also indicated in this and other experiments by a complete absence of trend in the value of (33/31) as measured for samples withdrawn at intermediate time intervals.

The possibility of acid catalysis of oxygen exchange was explored in a series of experiments in which NO was brought into contact with H_2^{18}O solutions of HCl (introduced as purified HCl gas). No oxygen exchange was detectable in these experiments within error of measurement. The most concentrated HCl solution employed was 4.4 M, in an experiment involving 24 hr of contact between NO and solution.

A gas-phase experiment was conducted in which H_2^{18}O vapor at 24 Torr and ^{15}NO at 300 Torr were mixed in a vessel and held at 25°. After 18 days a sample of NO was withdrawn and found to exhibit a 33/31 ratio of 0.00210, relative to a "standard" value of 0.00209.

Since there is no observed exchange of oxygen between NO and H_2O , it is concluded that NO exists in essentially unaltered molecular form in aqueous solution and that it is not the chemical anhydride of $\text{H}_2\text{N}_2\text{O}_3$. This conclusion depends upon an estimation that molecular interaction which does not lead to oxygen exchange is improbable and is supported by spectroscopic evidence.⁹ Reports concerning the existence of $\text{H}_2\text{N}_2\text{O}_3$ in aqueous NO solution, $\text{H}_2\text{N}_2\text{O}_3$ and its anions as intermediates in aqueous solution processes involving NO, the conductivity of NO solution, and similar phenomena were probably based upon observations employing incompletely purified NO, insufficiently outgassed H_2O , or both. The pH of NO solution should be neutral, and reports to the contrary are probably based upon observations involving incomplete exclusion of O_2 or CO_2 .

II. Catalysis by Dissolved NO_2 .—In performing the experiments described above, it is found that insufficient outgassing of the aqueous phase leads to oxygen exchange. It was also found important to achieve good NO- H_2O separation during sampling in order to elimi-

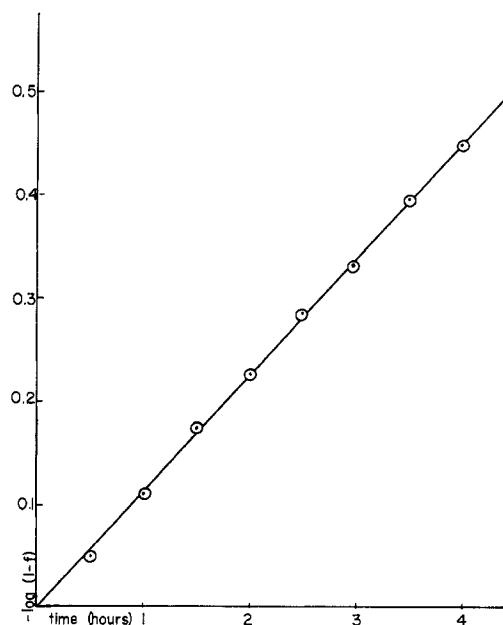


Figure 1.—Oxygen exchange between NO and H_2O catalyzed by dissolved NO_2 . Conditions: 2.5×10^{-6} mol of NO_2 in 10 ml of H_2O , 0.0088 M in HCl, 25°.

nate the possibility of exchange occurring subsequent to sample withdrawal. Incomplete exclusion of molecular oxygen from the system is responsible for the exchange observed in these instances, as was demonstrated in the case of the gas-phase experiment described above: after 18 days of NO- H_2O contact without measurable exchange, O_2 at a partial pressure of 8.5 Torr was introduced to this system. An NO sample withdrawn 25 min later was found to have a 33/31 ratio of 0.3387, corresponding very nearly to isotopic equilibrium for the quantities involved.

The fact that molecular oxygen is capable of stimulating oxygen exchange in the H_2O -NO systems must be interpreted in terms of the NO_2 that will be formed under these conditions and therefore by implication its hydrolysis products nitric and nitrous acids. Experiments were carried out in which small, volumetrically measured quantities of NO were treated with excess O_2 , and the resultant NO_2 was transferred by distillation, following removal of excess O_2 , to a reaction cell containing an outgassed charge of H_2^{18}O . NO_2 was then hydrolyzed, NO was admitted to the cell, and gas samples were withdrawn at intervals. Excellent exchange curves were obtained in this way, as exemplified by Figure 1. In this example 2.52×10^{-6} mol of NO_2 was dissolved in 10 ml of H_2O . (This particular solution was also 0.0088 M in HCl, although acidification was not essential to exchange.) Agitation of the solution to promote NO_2 hydrolysis was conducted for 1 hr before the admission of NO.

The exchange function f , plotted in the form $-\log(1-f)$ vs. time in Figure 1, is related to experimental quantities as shown by

$$f = \frac{\left(\frac{33}{33+31}\right)_t - \left(\frac{33}{33+31}\right)_0}{\left(\frac{33}{33+31}\right)_\infty - \left(\frac{33}{33+31}\right)_0}$$

(9) R. Grajower and J. Jortner, *J. Am. Chem. Soc.*, **85**, 512 (1963).

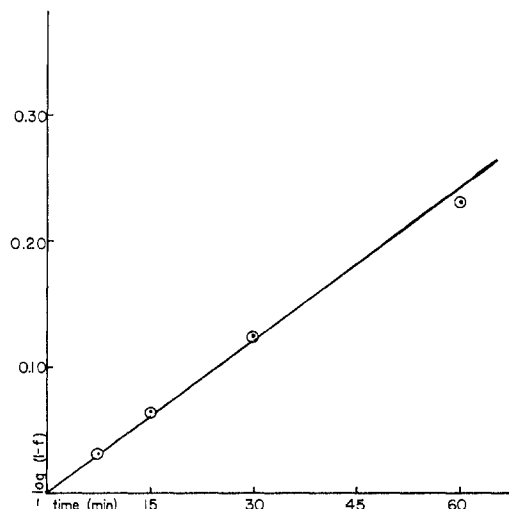


Figure 2.—Oxygen exchange between NO and H₂O. Conditions: [HNO₂] = 0.00144 M; [NO₂⁻] = 0.0226 M, 25°.

In the exchange equation

$$-\log(1-f) = \frac{[\text{H}_2\text{O}] + [\text{NO}]}{[\text{H}_2\text{O}][\text{NO}]} R t$$

since H₂O molecules greatly outnumber NO molecules

$$\frac{-d \log(1-f)}{dt} = \frac{R}{[\text{NO}]} = R'$$

the slope of the straight line in Figure 1. The concentration of NO in the aqueous phase is its solubility (about 1.7×10^{-3} M at 25° and $P_{\text{NO}} = 1$ atm),¹⁰ and since it varies proportionally with pressure, the quantity R' can be constant as observed only if the intrinsic rate R is proportional to [NO]. Since in the experiment shown in Figure 1 and others like it the partial pressure of NO is reduced by about 2% for each sample withdrawn, the straight-line exchange function observed shows that the exchange process is first order with respect to NO. This conclusion was tested in other experiments by alteration of P_{NO} by as much as 50% in single sample withdrawals, which were similarly found not to cause changes of slope in the corresponding exchange plots.

The half-time of exchange for the experiment reported in Figure 1 is about 2.5 hr. The magnitude of R' as measured from the plot is not a value intrinsic to the aqueous-phase process, however, since dissolved NO is maintained in equilibrium with an extensive gas-phase reservoir of NO gas and the observed rate must therefore be a function of the relative volumes of liquid and gas phases; to compare rates measured in different configurations it is necessary to multiply observed rates by the ratio of total moles to dissolved moles of NO.

Variations in phase-mixing speed were carried out in exchange systems employing dissolved NO₂ as catalyst, showing that at the slow exchange rates involved, relatively slow stirring can be employed without reaching a phase-exchange rate limitation. This made it possible to employ the cell with Teflon stirring bar, as described earlier, for experiments involving nonvolatile solutes.

III. Noncatalytic Effect of Dilute HNO₂.—Concentrated HNO₃ is known to cause oxygen exchange be-

(10) L. W. Winkler, *Ber.*, **34**, 1409 (1901).

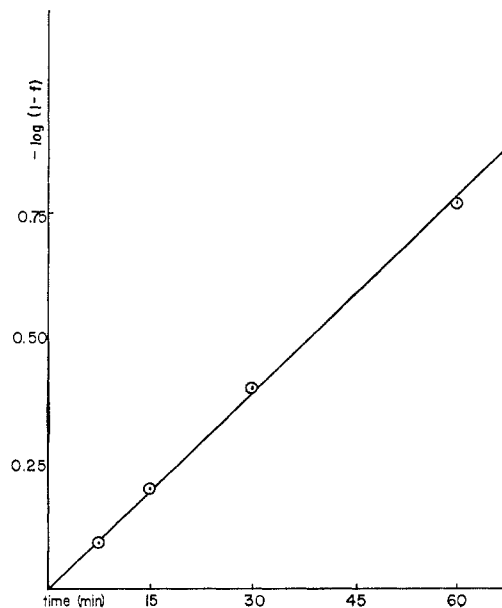


Figure 3.—Nitrogen exchange between NO and NO₂⁻, using the same system as described for Figure 2.

tween NO and H₂O,^{11,12} and since HNO₃ is a product of NO₂ hydrolysis, an experiment was performed to determine whether it is active in the dilute concentration range employed in these experiments. No oxygen exchange was detected following 3 hr of contact between NO and a solution of 0.0024 M HNO₃. Since the solution reported in Figure 1 would presumably be 0.00125 M in HNO₃ and equally concentrated in HNO₂, it is implied that HNO₂ is responsible for the exchange process observed.

IV. Catalysis by HNO₂ and Simultaneous Nitrogen Exchange.—To investigate the NO–H₂O oxygen-exchange catalysis by HNO₂, experiments were carried out in solutions containing NO₂⁻ and a small quantity of strong acid added to establish a known concentration of HNO₂. HClO₄ was used in several experiments, but to avoid extensive outgassing subsequent to makeup of the solution, which could lead to decomposition of HNO₂, in most experiments measured quantities of HCl gas were introduced to the cell after outgassing and just prior to initiation of the exchange reaction. In these experiments the use of an ¹⁵N-labeled gas phase and NO₂⁻ at natural isotopic abundance made it possible to follow the exchange of nitrogen between NO and NO₂⁻ simultaneously with the observations of NO–H₂O oxygen exchange.

Good exchange curves were obtained for both the N- and O-exchange processes, as illustrated in Figures 2 and 3. Employing the criterion stated previously, both processes are kinetically first order in NO. The most arresting feature of these experiments, however, is that in every observed case the nitrogen-exchange process is significantly more rapid than oxygen exchange. In the case illustrated (Figures 2 and 3) the ratio of rates is somewhat greater than 3, and the range of rate ratios observed generally lay between 3 and 6. (These may

(11) T. I. Taylor and J. C. Clarke, *J. Chem. Phys.*, **31**, 277 (1959).

(12) S. C. Saxena and T. I. Taylor, *J. Phys. Chem.*, **66**, 1480 (1962).

be taken to be minimum values, however, since it is not certain that phase mixing was adequate for the more rapid nitrogen-exchange process; the rates observed for nitrogen could be less than true exchange rate values, which would make the nitrogen to oxygen exchange rate ratios greater than observed by this method.)

The exchange of oxygen between H_2O and NO_2^- has been investigated previously.^{13,14} It seems plausible that the H_2O -NO exchange may be a similar process with respect to the transfer of oxygen between H_2O and NO_2^- , but since there is no direct interaction between NO and H_2O , the ultimate transfer of aqueous-phase oxygen to NO must occur through interaction with a dissolved, nitrogen-containing species. Given the observed first-order dependence of the over-all process upon NO, the latter could be considered a catalyst to the H_2O - NO_2^- exchange if its mechanism is otherwise unchanged by the presence of NO, a point that awaits further investigation.

The interesting fact that NO- NO_2^- nitrogen exchange is more rapid than NO- H_2O oxygen exchange in a single system suggests that there may be a direct attack of NO on NO_2^- . If so, diatomic NO units would undergo continuous exchange with nitrite ions, and the rate of appearance of ^{18}O in the gas phase would be limited by the rate of its exchange in the solution between H_2O and NO_2^- . To test this idea, an experiment was carried out in which NO_2^- was labeled with ^{18}O before NO was admitted. This was accomplished by addition of a measured quantity of HCl to an out-gassed solution of NO_2^- in H_2^{18}O and allowing H_2O - NO_2^- exchange to take place in the resultant HNO_2 solution during a period of 17 hr. NO was then admitted to the solution containing N^{18}OO^- and HNO_2 , and kinetic data were obtained in the usual way, with the result shown in Figure 4. As seen, the nitrogen-exchange curve is normal, although there is an intercept, probably caused by release of NO by disproportionation of HNO_2 during the long preexchange period. The oxygen-exchange plot, however, is characterized by continuous curvature. Curvature in an exchange plot could be caused by a change in chemical composition, but since no curvature was observed in similar experiments conducted without prelabeling, it is not thought to have occurred here. Rather, the result is readily interpreted in terms of an NO- NO_2^- interaction in which the rate of appearance of ^{18}O in the gas phase is limited by the rate of oxygen exchange between H_2O and NO_2^- which is in turn considerably slower than the NO- NO_2^- exchange. Thus at the outset of the exchange with pre-labeled N^{18}OO^- the apparent O-exchange rate is rapid, but falls off as NO_2^- becomes increasingly depleted in ^{18}O at a rate greater than that at which it can be restored by H_2O - NO_2^- exchange. This accounts for the appearance of continuous curvature in the O-exchange plot and is in accordance with the hypothesis of a direct attack of NO on NO_2^- .

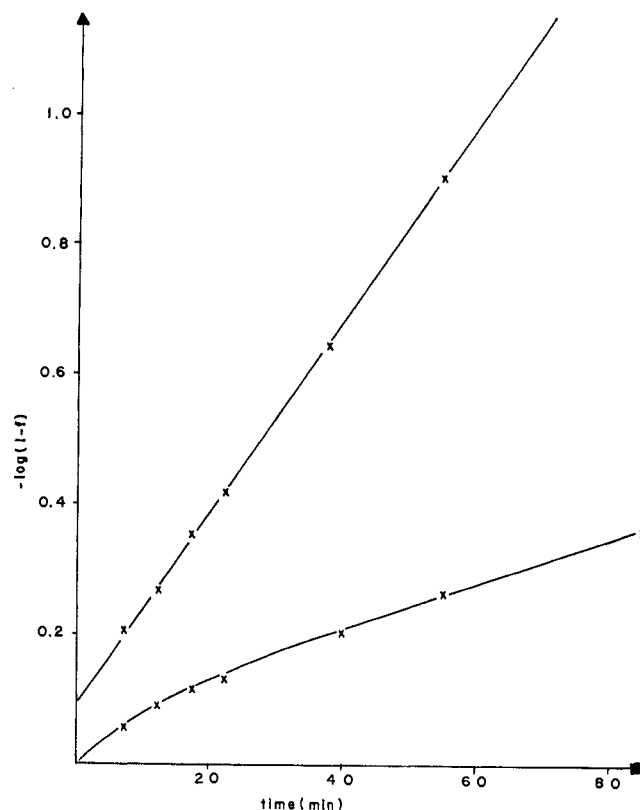


Figure 4. N exchange (upper curve) and O exchange (lower curve) in solution containing N^{18}OO^- . Conditions: $[\text{HNO}_2] = 0.00147$, $[\text{NO}_2^-] = 0.0226$, 25° .

It is certain, on the basis of results reported here, that N and O exchanges proceed *via* distinct mechanisms in this interesting system. Further investigation is in progress, in an effort to elucidate differences between the two exchange mechanisms in detail.

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Tellurium Tetrakis(tetramethylenedithiocarbamate)

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In the course of a study of the determination of tellurium by means of atomic absorption spectroscopy¹ we observed that a yellow microcrystalline substance was precipitated from mixtures of aqueous solutions of

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(13) M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6234 (1954).

(14) C. A. Bunton, D. R. Llewellyn, and G. Stedman, *J. Chem. Soc.*, 588 (1959).