957. *Oxygen Exchange between Nitric Acid and Water. Part I.*

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The exchange of oxygen atoms between nitric acid and water has been followed by using heavy oxygen as an isotopic tracer. At low acid concentrations the reaction is highly dependent upon " nitrous acid," but at higher nitric acid concentrations a reaction is observed in the absence of " nitrous acid." The reaction rate increases rapidly with increasing concentration of nitric acid. The mechanism of this exchange is discussed in detail in Part II (following paper).

THE exchange of oxygen atoms between inorganic oxy-acids and water has frequently been observed qualitatively by the use of ^{18}O. We now report the results of a study of the exchange of oxygen between nitric acid and water. The exchange has been followed over a range of nitric acid concentration, with the object of comparing, where possible, the rates of isotopic exchange with those of aromatic nitration.

A brief report of an exchange between nitric acid and water has been given by Klein and Friedel (*J. Amer. Chem. Soc.*, 1950, **72**, 3810), who separated the water from the nitric acid by distillation, and carried out a mass-spectrometric analysis directly upon the water. Such a method is unsuitable for a detailed kinetic investigation of the exchange.

The method used must permit a rapid stopping of all exchange, and allow isolation of either nitric acid or water, uncontaminated by the other, followed by a mass-spectrometric analysis of the sample. These criteria are satisfied by the method adopted : the exchange reaction was quenched in a definite amount of normal water, the nitric acid isolated as potassium nitrate, and the mass-spectrometric analyses carried out on oxygen gas liberated from the potassium nitrate.

It was necessary to demonstrate the absence of extraneous exchanges in this method of recovery; this was tested by two independent methods. First, mixtures of normal water and nitric acid were quenched in enriched water, and the potassium nitrate was isolated and decomposed in the normal way. The results of a typical experiment are outlined below: $[HNO_3] = 51{\cdot}87$ mol. %. Isotopic abundance of quenching water = 2·31 atoms % excess. Isotopic abundance of isolated potassium nitrate = 0·014 atom % excess. Extraneous exchange = 0·6 % dilution.

The second, and more generally applicable, test was made by comparing the isotopic abundance of the isolated potassium nitrate, after complete equilibration between normal nitric acid and enriched water, with that calculated from the known isotopic abundance of the water, and the relative concentrations of nitric acid and water. A typical result is given below:

$[HNO_3] = 66{\cdot}44$ mol. %. Initial isotopic abundance of water = 2·83 atoms % excess.

Time, min.		30	45	75
Isotopic abundance of KNO_3, atoms % excess	Obs.	0·410	0·410	0·411
	Calc.	—	0·408	—

These values suggest that effects due to differing normal isotopic abundances in nitric acid and water, or to isotope effects in the decomposition of the potassium nitrate, are not large, or are fortuitously self-cancelling. Such isotope effects were neglected in the calculation of rate data.

The Relation between Isotope Exchange and Chemical Reaction.—The generally accepted expression for the net rate of exchange of an isotopically labelled atom X* between two species AX_n and BX_m, in the absence of an appreciable "isotope effect," is given by

$$d[X^* \text{ in } AX_n]/dt = d[X^* \text{ in } BX_m]/dt = R(\beta - \alpha) \quad . \quad . \quad . \quad . \quad (1)$$

where α and β are the respective isotopic abundances, defined as

$$\alpha = [X^* \text{ in } AX_n]/n[AX_n] \text{ and } \beta = [X^* \text{ in } BX_m]/m[BX_m]$$

and $R = dX/dt$, or the actual rate of atomic transfer regardless of labelling. This, in the case of monatomic transfer, is identical with the rate of the chemical reaction responsible for it. In systems of constant chemical composition, (1) can be rewritten:

$$n[AX_n] \,.\, d\alpha/dt = -m[BX_m]d\beta/dt = R(\beta - \alpha) \quad . \quad . \quad . \quad . \quad (1a)$$

in which R is constant. This expression is equivalent to that deduced by Harris (*Trans. Faraday Soc.*, 1951, **47**, 716), and has been derived in several forms with varying degrees of generality (Duffield and Calvin, *J. Amer. Chem. Soc.*, 1946, **68**, 559; Harris, *loc. cit.*).

The "exchange rate constant," $k_{ex.}$, measuring the rate of approach of the isotopic abundance, α, to its value at infinite time α_∞ and given by

$$k_{ex.} = \frac{d}{dt}\left(\frac{\alpha}{\alpha_\infty - \alpha}\right) = -\frac{d}{dt}\ln(\alpha_\infty - \alpha) = -\frac{d}{dt}\ln(100 - \%\text{ completion}) \;. \quad (2)$$

may be related to R by a simple extension of Roberts and Urey's treatment (*J. Amer. Chem. Soc.*, 1939, **61**, 2580).

At equilibrium, in the absence of an appreciable isotope effect, the isotopic abundances in the various species must be equal, and since the total number of labelled atoms is constant:

$$n[AX_n]\alpha + m[BX_m]\beta = \{n[AX_n] + m[BX_m]\}\alpha_\infty$$

and

$$(\beta - \alpha) = [1 + n[AX_n]/m[BX_m](\alpha_\infty - \alpha) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From equations (2), (3), and (1*a*) we obtain

$$R = \frac{mn[AX_n][BX_m]}{n[AX_n] + m[BX_m]} \cdot k_{ex.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Using the experimentally more convenient quantity "excess abundance" above normal, and assuming that the normal distribution is the same for all species, we have $\alpha' = \alpha - \alpha_n$ and $\beta' = \beta - \alpha_n$, where α' and β' are the excess, and α_n the normal abundances respectively; and if AX_n is initially isotopically normal:

$$\alpha' = 0;\ \beta' = \beta_0 - \alpha_n,$$

The theoretical values for α' at equilibrium are given by

$$\alpha' = \beta_0'/(1 + n[AX_n]/m[BX_m]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the work reported, the initial labelling, of abundance β', was always in the water. Therefore the values of R are given by:

$$R = -\frac{3[HNO_3][H_2O]}{3[HNO_3] + [H_2O]} \cdot \frac{d}{dt} \ln(\alpha_\infty' - \alpha') \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

where

$$\alpha' = \beta_0'(1 + 3[HNO_3]/[H_2O]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

Discussion.—A preliminary kinetic investigation showed that the lower oxides of nitrogen, which can be analysed together as "nitrous acid," upon dilution with water, have a very marked catalytic effect, even in concentrations below 10^{-3}M. Such concentrations of nitrous acid can be produced by the slight decomposition which occurs when "pure" nitric acid is diluted with water. This powerful effect of nitrous acid makes it impossible for us to compare, even qualitatively, our results with those of Klein and Friedel (*loc. cit.*). These workers do not quote the concentrations of nitrous acid in their solutions, although, in the nitric acid range in which their experiments were carried out, the catalytic effect of nitrous acid is of prime importance. We find that, in the absence of nitrous acid, no conveniently measurable exchange between water and nitric acid occurs below a concentration of *ca.* 40 moles % of nitric acid.*

TABLE 1. *Run No.* 32.

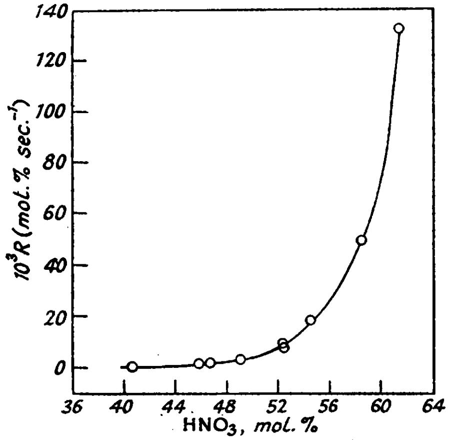
$[HNO_3] = 46{\cdot}77$ *mol* %.
$\beta_0' = 4{\cdot}37$ *atom % excess* O^{18}.
$\alpha'_\infty = 1{\cdot}202$ *atom % excess* O^{18}.

Time (hr.)	α'	$\log_{10}(\alpha'_\infty - \alpha')$ (exp.)	$\log_{10}(\alpha'_\infty - \alpha')$ (calc.) *
0	0·058	0·059	0·062
1	0·232	$\bar{1}$·986	$\bar{1}$·989
2	0·383	$\bar{1}$·913	$\bar{1}$·916
3	0·487	$\bar{1}$·854	$\bar{1}$·842
4	0·611	$\bar{1}$·772	$\bar{1}$·769
5	0·705	$\bar{1}$·697	$\bar{1}$·696
6	0·790	$\bar{1}$·615	$\bar{1}$·623

$R = 1{\cdot}81 \times 10^{-3}$ mol. % sec.$^{-1}$.

* Values calc. from the "least squares" straight line: $\log_{10}(\alpha'_\infty - \alpha') = 0{\cdot}062 - 0{\cdot}0732t$ (hr.).

Variation of exchange rate with nitric acid concentration.



Above this nitric acid concentration, an exchange occurs even with nitrous acid concentrations below our measurable limits, an increase in nitric acid concentration giving a very rapid increase in exchange rate, and within a comparatively short range of acid concentration the rate becomes too rapid for convenient measurement.

The data for a typical run are given in Table 1 and the effect of nitric acid concentration on rate is shown in the Figure.

The runs tabulated in Table 2 fall into two main sets. The first, in which water of $\beta_0' = 1{\cdot}785$ atoms % excess was used, were exploratory runs, each of four points. The

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* This effect of nitrous acid will be the subject of a later communication.

second set of runs carried out with water of $\beta_0' = 4{\cdot}37$ atoms % excess, consists of 7 or 8 points each. One run (at 40·34 mol. % HNO_3) was carried out with water of 11·4 atoms % excess.

TABLE 2.

Run	HNO_3, mol. %	β'_0 (atoms % excess)	$10^3 \times R$ (moles % sec.$^{-1}$)	Run	HNO_3, mol. %	β'_0 (atoms % excess)	$10^3 \times R$ (moles % sec.$^{-1}$)
25	45·85	1·785	1·39	32	46·77	4·37	1·81
27	49·03	,,	3.05	30	52·28	,,	7·85
26	52·23	,,	9·20	29	54·58	,,	18·1
28	58·58	,,	49·3	31	61·67	,,	132
				37	40·34	11·40	0·284

The nitrous acid values observed in all these runs were no higher than the blank of the analytical method, *ca.* 1×10^{-4}M; this blank depended upon the concentration of nitric acid.

EXPERIMENTAL

Preparation of Materials.—Enriched water. Water with the required enrichment of ^{18}O was prepared by fractional distillation of normal water in columns of the type described by Dostrovsky, Hughes, and Llewellyn (*Nature*, 1948, **161**, 858). It was purified by static distillation *in vacuo*, and its isotopic abundance (β_0') determined mass spectrometrically after equilibration with carbon dioxide gas, by Cohn and Urey's method (*J. Amer. Chem. Soc.*, 1938, **60**, 679).

Nitric acid. This was purified by vacuum distillation from sulphuric acid (Benford and Ingold, *J.*, 1938, 929), and preserved in the dark in stoppered tubes at −80°.

Kinetic Procedure.—The enriched water was weighed into a glass-stoppered tube, to this were added *ca.* 5 mg. of recrystallised sulphamic acid, and the water was partly frozen. Purified nitric acid, near its m. p., was added dropwise from a vacuum-jacketed weight pipette, with thorough mixing and occasional cooling in solid carbon dioxide slush. The sulphamic acid removed any nitrous acid formed on mixing with water, and had no observable effect on the rate.

After the temperature equilibrium was reached in a thermostat at 0°, portions of *ca.* 0·1 c.c. were withdrawn periodically, and quenched in 25 c.c. of cold water. The initial sample was taken at an arbitrarily chosen zero time.

The solution was titrated potentiometrically with standard potassium hydroxide, and a portion of the neutralised solution withdrawn for evaporation to dryness *in vacuo*. The remainder of the solution was analysed for nitrous acid.

The dry potassium nitrate was decomposed thermally *in vacuo*, and the isotopic abundance of the evolved oxygen gas determined mass-spectroscopically.

It was necessary to decompose exactly neutralised potassium nitrate; if the decompositions were carried out in the presence of potassium hydroxide erratic results were obtained, and apparently some of the oxygen evolved was derived from the potassium hydroxide.

Determination of Nitrous Acid.—The method used was a modification of the standard Griess–Ilosvay colorimetric method (Lunge and Swolf, *Z. angew. Chem.*, 1898, **7**, 348), devised with Dr. J. H. Ridd (Thesis, London, 1951). The diazotisation and coupling were carried out separately, at their appropriate pH's. By this procedure the colour developed rapidly and did not vary with time. A blank of *ca.* 1×10^{-4}M, in the original solution, possibly due to local formation of nitrous acid by the heat of dilution of the nitric acid, limits the accuracy of the determination of nitrous acid in nitric acid, but is probably common to all methods in which the nitric acid is diluted before determination.

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