an induced exchange does not exclude the existence of such intermediates. In order to detect induced exchange, two requirements have to be fulfilled:

(a) the XOOH should exchange with water at a reasonable rate; (b) it should exist in the system long enough for such an exchange to take place.

# The Exchange of Oxygen between Hydrogen Peroxide and Water in Nitric Acid Solutions

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The kinetics of isotopic exchange of $H_2O_2$ with water in nitric acid solutions have been studied at 60 and at 100°. The dependence of the rate of exchange on the concentrations of nitric acid, nitrate ions and perchloric acid suggests nitrogen pentoxide as nitrating agent. A simultaneous isotopic exchange between hydrogen peroxide and nitric acid has been observed; on the other hand, no exchange between water and nitric acid is induced by the hydrogen peroxide exchange. The mechanism of exchange postulates pernitric acid as intermediate: $N_2O_5 + H_2O_2^{**} \rightarrow HNO_3 + O_2N\overset{**}{O}OH$; $O_2N\overset{**}{O}OH + H_2\overset{*}{O} \rightleftharpoons O_2N\overset{*}{O}H + H\overset{\wedge}{O}OH$.

The isotopic exchange of oxygen between hydrogen peroxide and water was subject to a number of investigations[1] but was not detected until recently. A careful study of this exchange in aqueous solutions highly enriched in $O^{18}$ facilitated the determination of the upper limit of the specific rate of this exchange[2] $k < 7 \times 10^{-9}$ at 25°.

A hydroxide ion catalyzed exchange was also observed[2] in 1 $N$ NaOH with a rate constant of $1.1 \times 10^{-7}$ min.$^{-1}$ at 25°. This nucleophilic substitution on the O–O bond implies that this bond eventually may be polarized to $\overset{-\delta}{O}-\overset{\delta+}{O}$; this polarization, however, is a process of a very low probability. It seemed reasonable that if the O–O bond is polarized by the inductive effect of a substituent X to form $X\overset{-\delta}{O}\overset{\delta+}{O}H$, the O–O bond may be more vulnerable to a nucleophilic attack. Substituents having a strong negative inductive effect are for instants NO, Cl, $NO_2$ and $SO_3$; the corresponding hydroperoxides ONOOH and ClOOH are only intermediates in hydroperoxide oxidation-reduction reactions,[3,4] $O_2$NOOH–pernitric acid has been postulated in certain reactions,[5] persulfuric acid $O_3$SOOH, on the other hand, is a well established species. Isotopic oxygen exchange between hydrogen peroxide and water was observed on interaction of nitrous and hypochlorous acids with $H_2O_2$, but no quantitative conclusions could be derived owing to the transient nature of these hydroperoxides.[2] It was the purpose of this study to investigate the oxygen exchange between $H_2O_2$ and water in a system where a stable hydroperoxide may be formed even if at low concentrations. Nitric or sulfuric acid solutions of $H_2O_2$ may contain such stable hydroperoxides.

(1) E. R. S. Winter and A. V. A. Briscoe, J. Am. Chem. Soc., 73, 496 (1951); C. A. Bunton and D. R. Llewellyn, Research, 5, 142 (1952).

(2) M. Anbar, to be published.

(3) M. Anbar and H. Taube, J. Am. Chem. Soc., 76, 6243 (1954).

(4) L. Erdey and J. Inczedy, Acta Chim. Hung., 11, 125 (1956).

(5) W. C. Schumb, C. N. Satterfield, R. L. Wentworth, "Hydrogen Peroxide," A.C.S. Monograph Series No. 128, 1955, p. 665. Cf. H. H. Sisler, "Comprehensive Inorg. Chemistry," Vol. V, Sneed and Brasted, editors, D. Van Nostrand Co., New York, N. Y., 1956. p. 101.

## Experimental

$H_2O^{18}$ was supplied from the distillation plant of the Weizmann Institute. Nitrite free nitric acid was prepared by vacuum distillation over urea. Sodium nitrate, perchloric acid and sulfuric acid were all of analytical purity. Hydrogen peroxide used was Merck Superoxol, stabilizer free reagent.

The acid concentration was determined by acidimetric titration. The $H_2O_2$ was determined gasometrically after catalytic decomposition over platinum black.

Procedure.—Solutions of $H_2O_2$ in $HNO_3$ were placed in a thermostat at 60 ± 0.1° or at 100 ± 0.2°. Aliquots were taken at intervals and the $H_2O_2$ was decomposed on a vacuum line over platinum black. It was found[2] that platinum black does not induce any exchange between $H_2O_2$ and water. The gas was transferred into a glass tube with a break off seal and was submitted to the mass spectrometric analysis.

The isotopic composition of the water was determined for each reaction mixture by equilibrating an aliquot with $CO_2$ and analyzing the gas.

In experiments were the exchange reaction of nitrate ions was also followed, the nitrate was precipitated as $Ba(NO_3)_2$ in an alcoholic solution. The dried $Ba(NO_3)_2$ was heated with $NH_4Cl$ in excess in a sealed glass tube for 45 minutes at 400° to form $N_2O$ which was then analyzed.
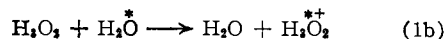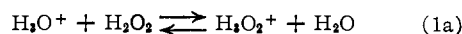
The mass spectrometric analysis was performed by a CEC model 21–401 Isotope Ratio Mass Spectrometer either by determining the ratio of masses 34/32 and 46/44 by the double collector or by determining the abundances of the individual masses.

The rate constants were derived graphically by plotting the logarithm of $A\infty - A$ vs. time, where $A$ is atom per cent. excess of $O^{18}$ in the sample.

## Results and Discussion

The isotopic exchange of oxygen between hydrogen peroxide and water was followed in perchloric, sulfuric and nitric acids; the results of these measurements at 60° are summarized in Table I.

Considering first the results in perchloric acid it seems that there exists no acid catalysed mechanism for the exchange. Such a mechanism might involve reaction 1b as the rate determining step, reaction 1a being a fast preëquilibrium.[6] Pre-

$$H_3O^+ + H_2O_2 \rightleftharpoons H_3O_2^+ + H_2O \qquad (1a)$$

$$H_3\overset{*}{O}_2 + H_2\overset{*}{O} \longrightarrow H_2O + H_3\overset{*+}{O}_2 \qquad (1b)$$

equilibrium 1a would require the specific rate con-

(6) M. Anbar, A. Loewenstein and S. Meiboom, J. Am. Chem. Soc., 80, 2630 (1958).

TABLE I

THE EFFECT OF ACID CONCENTRATION ON THE RATE OF $H_2O_2$-$H_2O$ ISOTOPIC EXCHANGE AT 60°

| | $H_0$ | (HNO₃), mole l.⁻¹ | $k$, min.⁻¹ | $k/$(H₂SO₄), mole⁻¹ l. min.⁻¹ × 10⁸ | $k/$(HNO₃)ᵢ², mole⁻² l.² min.⁻¹ × 10⁴ |
|---|---|---|---|---|---|
| 0.1 M HClO₄ | +1 | | 2.2 10⁻⁸ | | |
| 4.0 M HClO₄ | −1.72 | | 2.8 10⁻⁸ | | |
| 4.0 M H₂SO₄ | −1.85 | | 4.5 10⁻⁸ | 1.1 | |
| 6.0 M H₂SO₄ | −2.76 | | 5.5 10⁻⁸ | 0.9 | |
| 7.0 M H₂SO₄ | −3.32 | | 6.8 10⁻⁸ | 1.0 | |
| 11.2 M H₂SO₄ | −5.60 | | 1.1 10⁻⁷ | 1.0 | |
| 1.0 M HNO₃ | −0.18 | 0.022 | 1.0 10⁻⁷ | | 2.06 |
| 2.1 M HNO₃ | −0.7 | .115 | 1.5 10⁻⁶ | | 1.14 |
| 3.0 M HNO₃ | −1.02 | .285 | 5.5 10⁻⁶ | | 0.68 |
| 4.0 M HNO₃ | −1.32 | .600 | 1.7 10⁻⁵ | | 0.47 |
| 4.7 M HNO₃ | −1.50 | .850 | 8.3 10⁻⁵ | | 1.15 |
| 5.6 M HNO₃ | −1.70 | 1.43 | 1.8 10⁻⁴ | | 0.88 |
| 6.0 M HNO₃ | −1.79 | 1.71 | 1.7 10⁻⁴ | | .58 |
| 7.0 M HNO₃ | −1.99 | 2.52 | 2.7 10⁻⁴ | | .43 |
| 8.0 M HNO₃ | −2.10 | 3.52 | 6.9 10⁻⁴ | | .56 |
| 10.0 M HNO₃ | −2.45 | 5.90 | 2.9 10⁻³ | | .83 |

stant to be dependent on the acidity function $H_0$. Examination of the data in Table I indicates no such correlation (the values of $H_0$ in Table I were taken or interpolated from Paul and Long[7]). Consequently, the exchange reaction in HClO₄ should be considered as an uncatalyzed interaction (1c), where water acts as a nucleophilic reagent.

$$\overset{*}{H_2O} + H_2O_2 \rightleftarrows H_2O + \overset{*}{H_2O_2} \qquad (1c)$$
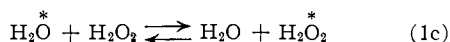
The isotopic exchange in sulfuric acid is a slow process (the half-life in 11.2 molar acid being over ten years at 60°), the rate constants are found proportional to sulfuric acid concentrations.

The range of H₂SO₄ concentration studies is not very extensive, as H₂O₂ undergoes fast decomposition in more concentrated H₂SO₄ solution under the experimental conditions. Because of this limited range of concentrations the first order dependence on H₂SO₄ is not conclusive. If the rate of "spontaneous" exchange is taken into account, the rate of the H₂SO₄ catalysed reaction is approximately proportional to the second power of H₂SO₄ concentration, which might then imply the participation of SO₃ in the exchange mechanism. This dependence on H₂SO₄ concentration may be explained by reaction 2a or by 2b. Qualitative observations of an exchange reaction of Caro's
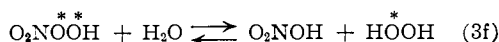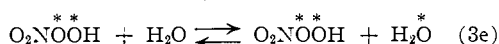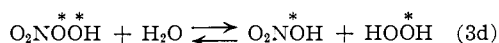
$$\overset{**}{H_2O_2} + H_2SO_4 \longrightarrow HO_3S\overset{*}{O}OH + H_2O \qquad (2a)$$

$$SO_3 + \overset{**}{H_2O_2} \longrightarrow H\overset{*}{O}\overset{*}{O}SO_3H \qquad (2b)$$

$$HO_3S\overset{*}{O}\overset{*}{O}H + H_2O \longrightarrow HO_3S\overset{*}{O}H + H\overset{*}{O}OH \qquad (2c)$$

$$HO_3S\overset{*}{O}\overset{*}{O}H + H_2O \longrightarrow HO_3S\overset{*}{O}OH + H_2\overset{*}{O} \qquad (2d)$$

$$HO_3S\overset{*}{O}OH + H_2O \longrightarrow HO_3SOH + H\overset{*}{O}OH \qquad (2e)$$

acid (H₂SO₅) with water in acid solutions have been reported,[8] this exchange may proceed either via reaction 2c or via reactions 2d and 2e. In order to extend Kolthoff's experiments[8] into higher

acid concentrations, where the SO₄ radical mechanism is unlikely, potassium persulfate was hydrolysed for 15 minutes in 14.4 N sulfuric acid in 82% $H_2O^{18}$ at 100°; the reaction mixture was then decomposed over Pt black at room temperature for 5 minutes and the evolved gas was analyzed; it contained 13.82 atom per cent. O¹⁸. This result suggests that reaction 2c is the exchange step on hydrolysis, because an exchange via reactions 2d and 2e would proceed at a much slower rate considering the exchange kinetics presented in Table I.

The isotopic exchange in nitric acid proceeds at a much higher rate than in perchloric or in sulfuric acids. The dependence of the rate of exchange on H₂O₂ concentration showed that it remains constant within ± 12% when H₂O₂ concentration was changed by a factor of ten. Moreover hydrogen peroxide concentration was decreasing constantly during the exchange experiments owing to its decomposition, still no deviation from the first order dependence was observed. These results imply a first order dependence on H₂O₂ concentration $R \propto k[H_2O_2]$. The dependence of the rate of exchange on the *stoichiometrical* concentration of HNO₃ shows approximately a fourth power dependence; it is hard however to suggest a mechanism with four molecules of nitric acid involved. Plotting log $k$ vs. $H_0$ in nitric acid yields a second order dependence, which implies[9] a rather improbable species ($H_3NO_3^{++}$) as intermediate. The next parameter examined was the concentration of *undissociated* nitric acid[10] $(HNO_3)_f$; values reported for 25° were used because it was hard to estimate dissociation constants at higher temperatures by extrapolation.[11,12] It was found that the specific rate constants are proportional to the second power of the concentration of undissociated nitric acid, $R = k[H_2O_3][HNO_3]_2^2$. As may be seen from Table I, this dependence holds throughout the whole range investigated, with rate constants changing by four orders of magnitude. The exchange mechanism suggested is therefore

$$H_3O^+ + NO_3^- \rightleftarrows HNO_3 + H_2O \qquad (3a)$$

$$HNO_3 + HNO_3 \rightleftarrows N_2O_5 + H_2O \qquad (3b)$$

$$N_2\overset{*}{O}_5 + H\overset{*}{O}OH \rightleftarrows HNO_3 + O_2N\overset{*}{O}\overset{*}{O}H \qquad (3c)$$

$$O_2N\overset{*}{O}\overset{*}{O}H + H_2O \rightleftarrows O_2N\overset{*}{O}H + H\overset{*}{O}OH \qquad (3d)$$

$$O_2N\overset{*}{O}\overset{*}{O}H + H_2O \rightleftarrows O_2N\overset{*}{O}OH + H_2\overset{*}{O} \qquad (3e)$$

$$O_2N\overset{*}{O}\overset{*}{O}H + H_2O \rightleftarrows O_2NOH + H\overset{*}{O}OH \qquad (3f)$$

The fast preëquilibria assumed are (3a), (3b) and (3c) and the rate determining step are either reaction 3d or reaction 3e followed by (3f). In order to test the participation of preëquilibrium 3a in the exchange mechanism, the effects of free nitrate ions as well as of a strong acid on the rate of exchange were examined. These results are presented in Table II. The concentration of un-

(7) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(8) I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 3055 (1951).

(9) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 983 (1957).

(10) O. Redlich and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 1833 (1943).

(11) O. Redlich, *Chem. Revs.*, **39**, 333 (1946).

(12) N. R. Rao, *Indian J. Phys.*, **17**, 295 (1943).

dissociated nitric acid in presence of $HClO_4$ and of $NaNO_3$ was calculated from the equilibrium constant for reaction 3a $K = 2.77 \times 10^{-2}$, which was calculated from the data of Redlich and Bigeleisen for 2 $M$ $HNO_3$. It is evident therefore that equilibrium 3a is involved in the exchange mechanism. The participation of $H_2NO_3^+$ which may also be formed from two molecules of nitric acid $2HNO_3 \rightarrow H_2NO_3^+ + NO_3^-$ is unlikely in view of the fact that nitrate ions increase the rate of exchange, whereas the concentration of $H_2NO_3^+$ is diminished in presence of $NO_3^-$.

TABLE II

THE EFFECT OF NITRATE IONS AND OF PERCHLORIC ACID ON RATE OF EXCHANGE (100°)

| | $(HNO_3)t$, mole l.$^{-1}$ | $k$, min.$^{-1}$ | $k/(HNO_3)t^2$ mole$^2$ l.$^2$ min.$^{-1}$ $\times 10^2$ |
|---|---|---|---|
| 1.0 $M$ $HNO_3$ | 0.022 | 1.5 $10^{-5}$ | 3.1 |
| 2.0 $M$ $HNO_3$ | .100 | 2.3 $10^{-4}$ | 2.3 |
| 2.0 $M$ $HNO_3$ + 2.0 $M$ $NaNO_3$ | .216 | 9.4 $10^{-4}$ | 2.0 |
| 2.0 $M$ $HNO_3$ + 2.0 $M$ $HClO_4$ | .216 | 1.1 $10^{-3}$ | 2.4 |
| 3.0 $M$ $HNO_3$ | .285 | 1.7 $10^{-3}$ | 2.1 |
| 6.0 $M$ $HNO_3$ | 1.71 | 4.5 $10^{-2}$ | 1.5 |
| 6.6 $M$ $HNO_3$ | 2.18 | 7.5 $10^{-2}$ | 1.6 |

Changing the concentration of $H_2O_2$ considerably did not change appreciably the rate of isotopic exchange, thus an exchange reaction zero order in $H_2O_2$ may be excluded. As the rate determining step involves a molecule of $H_2O_2$, reaction 3b must also be a preëquilibrium reaction. Reaction 3c, being an analogous step to the reverse of reaction 3b, may be considered as a fast reaction compared to reactions 3d or 3e; thus it is the stationary concentration of pernitric acid that determines the rate of exchange. Since there is no experimental value for the equilibrium constants of reactions 3b and 3c, no estimate can be made for the specific rate constant of the rate determining step.

If the step involving isotopic exchange is reaction 3d, then an isotopic exchange between hydrogen peroxide and nitric acid would be expected. In order to check on this, a kinetic experiment presented in Table III was carried out. Nitric acid at an isotopic concentration *lower* than that of the solvent was mixed with hydrogen peroxide at normal isotopic composition and the changes in the isotopic composition of nitric acid, hydrogen peroxide and water were followed.

From these results it is evident that as the $H_2O_2$ exchanges with the solvent, a decrease in the isotopic concentration of $O^{18}$ in the nitric acid is observed, which implies an exchange reaction between $H_2O_2$ and $HNO_3$. At the final stage the isotopic concentration of $O^{18}$ in $HNO_3$ increases again, owing to its equilibration with the solvent. Reaction 3f, on the other hand, would require nitric acid to exchange with water at least at the rate of

TABLE III

SIMULTANEOUS EXCHANGE OF HYDROGEN PEROXIDE WITH WATER AND WITH NITRIC ACID

| Time, min. | $(HNO_3) = 6.6\ N$ atom % $O^{18}$ in $H_2O$ | $(H_2O_2) = 1.5\ M$ Temp., 100° atom % $O^{18}$ in $H_2O_2$ | Atom % $O^{18}$ in $HNO_3$ |
|---|---|---|---|
| 0 | 38.2 | 0.21 | 36.8 |
| 15 | | 3.66 | 34.5 |
| 35 | | 8.60 | 33.0 |
| 57 | | 13.8 | 32.3 |
| 85 | 37.7 | | 34.2 |

the hydrogen peroxide exchange. It was found, however, that in nitric acid solutions above 4 $M$ the rate of hydrogen peroxide exchange with water exceeds that of nitric acid with water. In 6 molar nitric acid the rate of $H_2O_2$ exchange with water is 3 times faster than that of nitric acid with the solvent[13]; moreover, hydrogen peroxide was found to have no catalytic effect on the rate of $HNO_3$–$H_2O$ exchange.

From the rate constants at 60 and a 100° an activation energy of 34 kcal./mole for the exchange reaction may be derived. This value, however, has little meaning, because the temperature coefficient of the exchange reaction involves the temperature dependence of the preëquilibria; thus the measured activation energy is not necessarily the energy of activation of the rate determining step.

The mechanism of formation of $O_2NOOH$ may be considered as a nitration reaction of $H_2O_2$, the nitrating agent in this case being not the nitronium ion but nitrogen pentoxide.[14] This reaction may just as well be looked at as a nucleophilic substitution on $N_2O_5$, a reaction which is analogous to its hydrolysis.

Reactions 3d and its analogous reaction 2c are nucleophilic substitution reactions on the peroxide oxygen. This means that the O–O bond undergoes polarization by the substituting group X forming $\overset{\delta_-}{X}O–\overset{\delta_+}{O}H$. This type of polarization is favored by the negative inductive effect (–I) of the group X. The relative inductive effect of the $SO_3$ group is smaller than that of $NO_2$,[15] thus the nucleophilic substitution by water on $O_2NOOH$ proceeds at a faster rate than that on $O_3SOOH$. Attempts to detect a nucleophilic substitution by $HSO_4^-$ on $O_3SOOH$ have failed,[16] probably because of the very low nucleophilic reactivity of the bisulfate ion. On the other hand induced isotopic exchange between hydrogen peroxide and water by hydroperoxides of transient nature[2] demonstrates other cases analogous to reactions 2b and 3d.

(13) M. Anbar and S. Guttmann, to be published.
(14) C. K. Ingold, "Substitution at Elements other than Carbon," Weizmann Science Press, 1959.
(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, Ch. 2,6.
(16) G. Levey, D. R. Campbell, J. O. Edwards and J. MacLachlan, J. Am. Chem. Soc., 79, 1797 (1957).