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Induced Oxygen Exchange Between Hydrogen Peroxide and Water

By M. Anbar

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An induced isotopic exchange of oxygen between H_2O_2 and water was observed on interaction of H_2O_2 with OCl⁻, IO_4^- MnO₄⁻, Fe⁺², Fe⁺³ and Ce⁺⁴ as well as with NO₂ and NO₂⁻. No induced isotopic exchange between different H_3O_2 molecules was detected. The formation of peroxy-complexes of the type XOOH is suggested which facilitates the isotopic exchange with water

$XOH + HOOH \rightleftharpoons XOOH + H_2O$; $XOOH + H_2O^* \rightleftharpoons HOOH + XOH$.

The reactions between hydrogen peroxide and various oxidants and reductants as well as the catalytic decomposition of H_2O_2 have been extensively studied using O^{18} as a tracer.¹⁻⁴

In these experiments H₂O₂ solutions of normal isotopic composition in water enriched in O¹⁸ were subjected to reaction with various reagents and the isotopic composition of the evolved oxygen was determined. In the cases cited water of low O18 content was used; thus it was hard to detect in the evolved gas, within the experimental error, any oxygen originating from the solvent. In this study H_2O^{18} highly enriched in O^{18} (~90% O^{18}) was used as a solvent, the sensitivity of detection of oxygen from the solvent consequently was increased by two orders of magnitude. Further, $\rm H_2O_2$ doubly labelled with $\rm O^{18}$ was mixed with hydrogen peroxide of normal isotopic composition, and the gas was analysed for $O_2^{16,18}$ molecules, which would be formed from two different molecules of H_2O_2 . The results showed that in certain reactions some of the oxygen evolved originates from the solvent; moreover, the residual H_2O_2 was found to have exchanged its oxygen with water to a certain extent.

Experimental

Materials.—H₂O¹⁸ (92–94% O¹⁸) supplied from the distillation plant of the Weizmann Institute was distilled 4–5

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 - (2) P. Baertschi, Experientia, 7, 215 (1951).

(3) M. Dole, D. P. Rudd, G. R. Muchow and C. Comte, J. Chem. Phys., 20, 961 (1952).

(4) C. A. Bunton and D. R. Llewellyn, Research, 5, 142 (1952).

times over alkaline permanganate and was tested by a conductivity bridge for purity. The $H_2O_2^{18,16}$ used was Merck Superoxol, stabilizer free reagent. $H_2O_2^{18,16}$ was synthesized as follows: a sodium mirror was formed by vacuum evaporation on the internal surface of a glass reaction vessel; next, excess $O_2^{18,18}$ was introduced and the vessel was warmed to some 200°. After making sure that all the sodium had reacted to form Na₂O₄, the vessel was opened and washed with a cooled 1 M H₂SO₄ solution in water of natural isotopic composition. Subsequently the H₂O₂^{18,18} was distilled off under vacuum together with most of the water (H₂O¹⁶). All other reagents were determined by a Metrohm type El48C potentiometer using a type U combined microelectrode, which has a minimal error in alkaline solutions.

Procedure.—Hydrogen peroxide and the respective reagents were placed in the different compartments of a Y shaped mixing vessel adapted with a vacuum stopcock and a ground joint connection to a vacuum line. After degassing on the vacuum line by consecutive freezing and melting, the solutions were mixed and allowed to react. After the reaction was completed, the evolved gas was subjected to mass spectrometric analysis.

In some cases where some of the H_2O_2 was not totally decomposed, either owing to its being in excess or because the reaction was stopped before coming to completion (see Table I), the residual reaction mixture was transferred into another reaction vessel and was decomposed over platinum black. As it will be shown later, over 99.99% of the oxygen evolved over Pt black originates from the H_2O_2 , and no "scrambling" between the oxygens of different molecules of H_2O_2 occurs under these conditions. The mass spectrometric analysis was performed by a CEC Model 21-401 Isotope Ratio Mass Spectrometer either by determining the ratio of the masses 34/32 by the double collector or by determining the abundances of the individual masses from 32 to 36, as well as masses 28 and 40 (to check on air contamination).

Results and Discussion

1. Isotope Exchange Between Hydrogen Peroxide and Water in the Presence of H_3O^+ and

OH⁻.—The isotopic composition of $H_2O_2^{16,16}$ in $\rm H_2O^{18}~(92\%~O^{18})$ did not undergo any change in 1 N HClO₄ at 25° within 10 days. This result implies that the specific rate of exchange is smaller than 7×10^{-9} min.⁻¹ at 25° .

In the alkaline range a 1 N NaOH solution of $0.1 M H_2O_2$ in H_2O^{18} was kept at 25° for 11 days in a polyethylene vessel, 14% of the H_2O_2 had decomposed during this period. The H₂O₂ exchanged with the water $(92\% O^{18})$ at a specific rate of $1.1 \times 10^{-7} \text{ min.}^{-1}$.

These results imply a half life of over 200 years for the spontaneous exchange of H_2O_2 with water. On the other hand there is an indication for a nucleophilic substitution mechanism, which means that the OO bond of H_2O_2 may eventually undergo

an HO-OH polarization. This reaction is, however, an extremely slow process.

2. Oxidation of $H_2O_2^{16,16}$ in H_2O^{18} by Various Reagents and Catalysts.— $H_2O_2^{16,16}$ in enriched H_2O^{18} (92-94% O^{18}) was mixed with various reagents forming oxygen by oxidation or by catalytic decomposition. The oxygen evolved was analysed for the mass ratio 34/32, and this analytical method was sensitive to detect one part in 10000 of oxygen originating from the water. Isotopic fractionation would account for changes in the isotopic composition of the evolved gas within 5%of the natural abundance, this would introduce an error of 0.01% in the estimated induced exchange with the solvent. It should be remembered that isotopic fractionation results in decrease of the abundance of $O_2^{16, 18}$ in the evolved oxygen whereas an induced exchange from the solvent obviously increases it.

Several other reactants produced no induced exchange in the evolved O₂: platinum black, lead dioxide, silver oxide, manganese dioxide, alkaline ferricyanide, bichromate in acid solution, brominebromide at pH = 4, iodine-iodide at pH = 4, chloroauric acid, as well as iodate in acid solution. Ferrocyanide at pH = 1 and 3 and sulfite both in acid and alkaline solutions failed to show any induced exchange in the residual hydrogen peroxide.

Another series of reagents including ferric and ferrous ions, ceric ion in strongly acid solution, permanganate in acid, periodate in neutral solution, hypochlorite and hypobromite in alkaline solutions, nitrogen dioxide in neutral and acid solutions as well as nitrite in acid solution showed induced exchange both in the residual hydrogen peroxide and in the O2 oxygen evolved. Representative results of these experiments are described in the following sections.

3. The Induced Exchange by Hypochlorite Ions in Alkaline Solution.—The results of the $OC1^-$ induced exchange in $0.2 N OH^-$ solution at various concentrations of H2O2 and OC1- and in presence of Cl⁻, Br⁻ and NO₂⁻ ions are summarized in Table I. The results in Table I are presented in terms of per cent. excess which may be converted into per cent. exchange by dividing by the factor 0.82 in order to normalize to 100%O¹⁸. From the data it may be seen that the induced exchange in the oxygen evolved upon oxi-

Induced Exchange in 0.2 N OH⁻ Solution of H₂O¹⁸ $(82\%~{\rm O^{18}})$ by Hypochlorite Ions in Presence of Cl-, Br - AND NO. - IONS

			102 10		
(H2O2), mole l. ⁻¹	(OCl ⁻), mole 1. ⁻¹	Additive	(Addi- tive) mole 1. ⁻¹	% O2 ^{16,18} excess ^a in O2 evolved	% H2O2 ^{16, 18} excess ^a in H2O2 residue
0.14	0.07			0.325	0.024
.14	.28			1.215	
.28	.07			0.132	0.007
.028	. 028	• • •		. 559	. 163 ^b
.14	.07	C1-	0.1	. 322	.022
.14	.07	C1-	. 5	. 301	.021
.14	.07	Br-	.1	.058	.003
.14	.07	NO_2^-	. 1	.040	.009
.14	.07	NO2-	.5	.022	Nil
a %O₂ ¹⁶ ,	¹⁸ escess	$=\frac{\overline{34}/\overline{32}}{2+\overline{2}}$	$\times 100$	- 0.200.	^b Oxidation

reaction stopped at 50% of completion.

dation of H_2O_2 is higher than the exchange induced in the residual H_2O_2 increases with the relative in the residual H_2O_2 . The induced exchange both in the evolved oxygen and excess of OCI- and with dilution of the reagents. Chloride ions have little effect on the induced exchange whereas bromide and nitrite ions reduce it. Changing alkalinity of the solution showed a six-fold increase in the induced exchange on decreasing OH⁻ concentration from 5 to 0.5 molar.

In order to determine the source of the oxygen which appears in the evolved O_2 and in the H_2O_2 , parallel runs were performed at $0.2 N \text{ OH}^-$ with OCl- of normal isotopic composition and with $O^{18}Cl = 90\%$ enriched in O^{18} . No oxygen exchange occurs at this alkalinity between OCl- and water.⁵ No oxygen from the O¹⁸Cl⁻ was detectable in the O_2 or in the residual H_2O_2 when the reaction was carried out in H₂O¹⁶ and no difference in the isotopic composition of O_2 and H_2O_2 was observed when H_2O_2 in H_2O^{16} interacted either with $O^{16}Cl^{-1}$ or with O18C1-.

It is suggested that HOOCl which may be formed on H₂O₂-HOCl interaction as an intermediate⁶ forms on hydrolysis hydrogen peroxide that may have exchanged with the solvent.

$$HOOCI + H_2O^* \xrightarrow{*} HOCI HOOH$$
 (1)

This cleavage of the O-O bond by a nucleophilic attack of water is facilitated by the negative inductive effect of the chlorine on this bond. Reaction 1 is analogous to the hydrolysis reaction of pernitric acid which was found to induce a similar isotopic exchange.7

The effects of changing concentrations of hydroxyl, bromide and nitrite ions and of hydrogen peroxide on the extent of induced exchange are consistent with the assumption of HOOCl as intermediate.

4. The Induced Exchange by Periodate and Permanganate Ions.—The results of the interaction between H_2O_2 and periodate in presence of chloride,

(5) M. Anbar and H. Taube, J. Am. Chem. Soc., 80, 1073 (1958).
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TABLE II

Гне	' NDUCED	Exchange	ON	INTERACTION	BETWEEN	H_2O_2
	and IO_4	- ат <i>р</i> Н =	7 in	82% H ₂ O ¹⁸	Solutions	
				(Addi-		

(H ₂ O ₂), mole 1. ¹	(IO ₄ -), mole 11	Additive	tive), mole 1. ⁻¹	% O2 ^{16, 18} excess	% H2O2 ^{16,18} excess
0.14	0.07			3.40	0.080
.48	.24			2.35	.022
.14	.14			3.22	.085ª
.07	.28			5.93	
.14	.07	C1-	0.1	1.64	0.045
.14	.07	C1-	. 5	0.39	0.027
.14	.07	Br ~	. 1	.075	Nil
.14	.07	Br-	.5	.012	Nil
.14	.07	No_2^-	.1	.121	Nil
. 14	.07	NO_2^-	.5	.063	Nil
a D		1 10007 -	cr 1		

^a Reaction stopped at 30% off completion.

bromide and nitrite ions are summarized in Table II.

In the hydrogen peroxide-periodate reaction similar to the interaction with OCl⁻, the induced exchange in the residual H_2O_2 is smaller than that in the evolved O_2 and both decrease with H_2O_2 concentration. Chloride, bromide and nitrite ions decrease this induced exchange considerably; the two last ions inhibit the induced exchange in the residual H_2O_2 entirely.

It could not be determined whether the labelled oxygen evolved originates from the water or from the periodate ion, since the rate of oxygen exchange between IO_4^- and water is fast.⁸ The induced exchange was found to increase 0.25% at pH 4.8 to 10.1% at pH = 7.2 and further down to 6.7% at pH = 9.

There is no independent experimental evidence for the existence of O_2IOOH but its formation seems rather likely and it may be of an analogous structure to that of O_2NOOH .⁷ The reactions of O_2IOOH are unknown as well as their *p*H dependence, thus it is hard to give any interpretation to the *p*H dependence of the induced oxygen exchange by periodate ions.

Permanganate ions in acid solutions were found to induce an oxygen exchange similarly to periodate, though to a smaller extent, thus we may postulate similar mechanisms for both oxyanions.

5. Induced Exchange by Nitrogen Dioxide and by Nitrous Acid.—Nitrogen dioxide and nitrous acid were found to induce oxygen exchange between H_2O_2 and water.

Nitrogen dioxide (200 mm.) was introduced into 0.2 N H₂O₂^{16,16} solutions in H₂O¹⁸ (82% O¹⁸) at pH = 12 and at pH = 6. After absorption of the gas, the residual H₂O was decomposed over Pt black. An induced exchange was observed at both acidities. The induced exchange observed in the alkaline region was 0.10% and that in the neutral region 0.52%.

Introduction of nitrite ions into acid solutions of H_2O_2 yielded, besides a quantitative oxidation of the nitrite present, also an induced isotopic exchange in the residual H_2O_2 . This induced exchange proceeds to a further extent with increasing acidity. At pH = 3.0 an exchange of 0.04%was observed as compared to a 5% induced ex-

(8) M. Anbar and S. Guttmann, J. Am. Chem. Soc., 83, 781 (1961).

change under similar conditions at pH = 1.0. The exchange induced by nitrogen dioxide and by nitrous acid is again attributed to their corresponding hydroperoxides.

The formation of O_2NOOH^- may be analogous to the formation of ONOOH which has been experimentally demonstrated.⁹

6. The Induced Exchange by Ceric, Ferrous and Ferric Ions.—The effects of Ce^{+4} , Fe^{+3} and Fe^{+2} on the isotopic composition of the evolved O_2 and of the residual H_2O_2 presented in Table III show trends similar to those of OC1⁻, IO_4^- and MnO₄⁻.

TABLE III INDUCED EXCHANGE BY CERIC, FERRIC AND FERROUS IONS IN H_2O^{18} (80% O^{18})

(H ₂ O ₂), mole 1. ⁻¹	Re- agent	(Re- agent) mole 1. ⁻¹	Acidity (H ₃ O ⁺), mole 1. ⁻¹	Additive	O2 ^{16,18} % excess	H2O2 ^{16, 18} % excess
0.18	Ce+4	0.11	1.0		0.140	
.71	Ce+4	.14	1.0		.081	
. 10	Ce+4	.23	1.0		.112	
.028	Ce+4	.033	1.0		.216	
. 33	Fe+8	.24	0.013		.060	
.037	Fe ⁺³	.027	0.013		.142	
.18	Fe++	.11	1.0		Nil	Nil
.12	Fe++	.10	0.1			0.040
.27	Fe ⁺⁺	.17	.013		0.012	.150
. 13	Fe++	.083	.013		. 110	.220
. 83	Fe++	.25	.001		.036	.096
.14	Fe ⁺⁺	.04	.001		.083	
.20	Fe ⁺⁺	.20	.0003		.043	.110
. 13	Fe ⁺⁺	.07	.013	0.08Br-	Nil	
. 13	Fe++	.08	.013	.08C1-	0.012	
.13	Fe ⁺⁺	.04	.001	.05Br-	0.022	

The induced exchange increases at lower concentrations of the reagents and at lower relative concentrations of H_2O_2 . In the case of ferrous ions an increase in acidity reduces the induced exchange. It should be noted that the induced exchange in the H_2O_2 exceeds that in the evolved O_2 .

Chloride and bromide ions inhibit the induced exchange almost entirely.

The general trend observed in the behavior of the hydrogen peroxide-hypochlorite and iodate reactions is followed also in the case of ferrous, ferric and ceric ions. It may be assumed, therefore, that the hydroperoxides $FeOOH^{++}$, $FeOOH^+$ and $CeOOH^{+3}$ are formed as intermediates. Complexes of this type have been postulated and even demonstrated spectrophotometrically¹⁰; thus the results may be considered as further evidence for their existence. It should be noted that $FeOOH^+$ does not yield oxygen on decomposition; this may be the reason that on decomposition of H_2O_2 with Fe^{++} the induced exchange observed in the residual H_2O_2 exceeds that of the evolved oxygen.

7. Decomposition of Mixtures of $H_2O_2^{16,16}$ and $H_2O_2^{18,18}$ by Various Reagents.—A series of reagents were examined for possible production of

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 (10) M. L. Kremer and G. Stein, Trans. Faraday Soc., 55, 959
 (1959). E. Abel, Monatsh., 87, 375 (1956). S. Baer and G. Stein, J. Chem. Soc., 3176 (1953). "scrambled" oxygen which originates from two different molecules of H_2O_2 . They were also tested whether they induce an exchange between *different* molecules of hydrogen peroxide yielding "scrambled" $H_2O_2^{16,18}$.

The first group of reagents tested were those which were found not to induce exchange and included: platinum black at pH = 1, 5 and 13, PbO₂, Ag₂O and MnO₂ at pH = 5; Fe(CN)₆⁻³ at pH = 13; Cr₂O₇⁻ in 0.2 N H⁺; Br₂⁻⁻Br⁻ and I₂-I⁻ at pH = 4 and HAuCl₄ in 0.5 N H⁺. No scrambling could be detected within 0.5%, neither in the evolved gas nor in the residual H₂O₂. The residue was decomposed over Pt black which was shown to evolve oxygen scrambled to an extent less than 0.1%.

These results imply that even in heterogeneous catalysis some kind of hydroperoxide must be formed and the oxygen evolved is a result of an interaction of a H_2O_2 molecule with the respective hydroperoxide. Any monomolecular dissociation of H_2O_2 on the surface of the catalyst would result in "scrambled" products.

The second group tested for scrambling included reagents which were found to induce exchange between H₂O₂ and water; in this case the results had to be corrected for the change in isotopic composition due to the exchange with the solvent. This group included MnO₄⁻ at 0.5 N H⁺, Fe⁺³ and Fe⁺² perchlorates at ρ H = 1.8, Ce⁺⁴ in 0.5 N H⁺, IO₄⁻ at ρ H = 3 and ρ H = 9 as well as OC1⁻ at ρ H = 13 and finally nitrite at ρ H = 1; in the last case only the residual H₂O₂ was examined. All reagents of the second group with the exclusion of OC1⁻ showed zero scrambling both in O₂ and in H₂O₂ with 1% accuracy, OC1⁻ on the other hand showed 4.2% scrambling in the evolved gas and no scrambling in the residual H₂O₂.

The most important conclusion of the negative results of these experiments is that the O-O bond remains intact during the oxidation-reduction reactions of both HOOH and XOOH. The fact that no "scrambling" was observed in the ferri-ferro reactions¹¹ does not exclude the participation of OH radicals in these reactions; although some scrambling might be expected due to reaction 2 which was ob-

$$\overset{\bullet}{\mathrm{OH}} + \mathrm{H}_{2}\mathrm{O}_{2} \xrightarrow{\longrightarrow} \mathrm{OH} + \mathrm{H}_{2}\mathrm{O}_{2}^{*} \tag{2}$$

served in X ray irradiated systems,¹² the fast reaction of OH radicals with Fe^{++} might compete efficiently with the OH-H₂O₂ reactions.

Conclusion

The extent of the induced oxygen exchange between hydrogen peroxide and water, described in this study, is rather small and its detection could be achieved only by the use of water highly enriched in O^{18} . The exchange reaction observed is a reaction of an intermediate of a very low concentration and of a short lifetime. The extent of exchange in most of the cases studied does not exceed 1% of total isotopic equilibrium and its

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determination was made possible only by the high sensitivity of the analytical method. It is obvious that under these conditions it would be hard to derive any quantitative rate laws for these exchange processes. The results of this study should be considered therefore as an observation of an effect in peroxide chemistry rather than an investigation of exchange kinetics.

Following the similar behavior of the induced exchange by the various reactants, it may be concluded: (a) the extent of the exchange in the evolved oxygen is greater than that in the residual H_2O_2 ; this would imply that the exchanged hydrogen peroxide is not the only precursor of the evolved oxygen; still both these labelled species may have a common precursor.

(b) The extent of exchange is diminished with the increase of H_2O_2 concentrations. At constant H_2O_2 concentration the exchange reaction is enhanced with increase of the concentration of the reactant. A plausible explanation of this effect may be that H_2O_2 interacts with the above mentioned precursor before it undergoes exchange with the solvent.

(c) Bromide and nitrite ions, as well as chloride ions in certain cases, decrease the oxygen transfer from the solvent. This observation may be again explained if we assume that these ions react with the precursor before any exchange with the solvent takes place.

It may be summarized that we assume the existence of a compound which is capable to exchange its oxygens with water, this may decompose to form either oxygen or eventually hydrogen peroxide. This compound may interact with hydrogen peroxide, bromide, nitrite and occasionally with chloride ions at a rate which is fast compared to the rate of the isotopic exchange process. Moreover, the oxygen exchange process seems to be slow compared to the rate of spontaneous decomposition of the precursor even at low H_2O_2 concentrations.

It is suggested here that this precursor is a hydroperoxy compound of the type XOOH which is formed as a product of the interaction of H_2O_2 with the respective reagent. The fact that XOOH exchanges with the solvent faster than HOOH may be explained by the inductive effect of X on the O-O bond. If X is an electron attracting group, this may polarize the OO bond to such an extent that the hydroperoxide may undergo a nucleophilic substitution by a water molecule, resulting in an isotopic oxygen exchange.⁷ This liability of XOOH

to undergo a nucleophilic substitution will increase with the strength of the negative inductive effect (-I) of X. Actually we find more extensive exchange reactions where X is NO or IO₂ compared to Cl or Fe⁺⁺. The reactivity of XOOH toward reductants will follow a similar sequence, thus will O₂IOOH be reduced by Cl⁻ whereas ClOOH remains intact.

The induced oxygen exchange suggests the existence of intermediates of the type XOOH in various reactions of hydrogen peroxide, yet the absence of 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.

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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: $N_2O_5 + H_2O_2^{**} \rightarrow HNO_2 + O_2NOOH; O_2NOOH + H_2O \Rightarrow O_2NOH + HOOH.$

The isotopic exchange of oxygen between hydrogen peroxide and water was subject to a number of investigations¹ but was not detected until recently. A careful study of this exchange in aqueous solutions highly enriched in O¹⁸ facilitated the determination of the upper limit of the specific rate of this exchange² $k < 7 \times 10^{-9}$ at 25°.

A hydroxide ion catalyzed exchange was also observed² in 1 N NaOH with a rate constant of 1.1×10^{-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 substit-

uent X to form XOOH, the O-O bond may be more vulnerable to a nucleophilic attack. Substituents having a strong negative inductive effect are for instants NO, Cl, NO₂ and SO₃; the corresponding hydroperoxides ONOOH and ClOOH are only intermediates in hydroperoxide oxidation-reduction reactions,^{3,4} O₂NOOH-pernitric acid has been postulated in certain reactions, 5 persulfuric acid O₈SOOH, 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 H2O2 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).

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(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

 $\rm H_2O^{18}$ 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 HNO₃ were placed in a thermostat at $60 \pm 0.1^\circ$ or at $100 \pm 0.2^\circ$. Aliquots were

Procedure.—Solutions of \hat{H}_2O_2 in HNO₃ were placed in a thermostat at 60 \pm 0.1° or at 100 \pm 0.2°. Aliquots were taken at intervals and the H_2O_2 was decomposed on a vacuum line over platinum black. It was found² 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 $Ba(NO_4)_2$ was heated with NH₄Cl in excess in a sealed glass tube for 45 minutes at 400° to form N₂O 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 O¹⁸ 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-

$$H_{3}O^{+} + H_{2}O_{2} \xrightarrow{} H_{3}O_{2}^{+} + H_{2}O \qquad (1a)$$

$$H_1O_1 + H_2O \longrightarrow H_2O + H_2O_2$$
 (1b)

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equilibrium 1a would require the specific rate con-(6) M. Anbar, A. Loewenstein and S. Meiboom, J. Am. Chem. Soc., 80, 2630 (1958).

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