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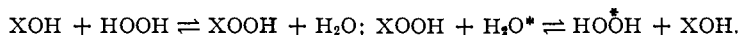
[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

### Induced Oxygen Exchange Between Hydrogen Peroxide and Water

BY M. ANBAR

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An induced isotopic exchange of oxygen between  $\text{H}_2\text{O}_2$  and water was observed on interaction of  $\text{H}_2\text{O}_2$  with  $\text{OCl}^-$ ,  $\text{IO}_4^-$ ,  $\text{MnO}_4^-$ ,  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$  and  $\text{Ce}^{+4}$  as well as with  $\text{NO}_2$  and  $\text{NO}_2^-$ . No induced isotopic exchange between different  $\text{H}_2\text{O}_2$  molecules was detected. The formation of peroxy-complexes of the type  $\text{XOOH}$  is suggested which facilitates the isotopic exchange with water



The reactions between hydrogen peroxide and various oxidants and reductants as well as the catalytic decomposition of  $\text{H}_2\text{O}_2$  have been extensively studied using  $\text{O}^{18}$  as a tracer.<sup>1-4</sup>

In these experiments  $\text{H}_2\text{O}_2$  solutions of normal isotopic composition in water enriched in  $\text{O}^{18}$  were subjected to reaction with various reagents and the isotopic composition of the evolved oxygen was determined. In the cases cited water of low  $\text{O}^{18}$  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  $\text{H}_2\text{O}^{18}$  highly enriched in  $\text{O}^{18}$  ( $\sim 90\%$   $\text{O}^{18}$ ) was used as a solvent, the sensitivity of detection of oxygen from the solvent consequently was increased by two orders of magnitude. Further,  $\text{H}_2\text{O}_2$  doubly labelled with  $\text{O}^{18}$  was mixed with hydrogen peroxide of normal isotopic composition, and the gas was analysed for  $\text{O}_2^{16,18}$  molecules, which would be formed from two different molecules of  $\text{H}_2\text{O}_2$ . The results showed that in certain reactions some of the oxygen evolved originates from the solvent; moreover, the residual  $\text{H}_2\text{O}_2$  was found to have exchanged its oxygen with water to a certain extent.

#### Experimental

**Materials.**— $\text{H}_2\text{O}^{18}$  (92–94%  $\text{O}^{18}$ ) supplied from the distillation plant of the Weizmann Institute was distilled 4–5

(1) E. R. S. Winter and A. V. A. Briscoe, *J. Am. Chem. Soc.*, **73**, 496 (1951).

(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  $\text{H}_2\text{O}_2^{16,18}$  used was Merck Superoxol, stabilizer free reagent.  $\text{H}_2\text{O}_2^{18,18}$  was synthesized as follows: a sodium mirror was formed by vacuum evaporation on the internal surface of a glass reaction vessel; next, excess  $\text{O}_2^{18,18}$  was introduced and the vessel was warmed to some  $200^\circ$ . After making sure that all the sodium had reacted to form  $\text{Na}_2\text{O}_2$ , the vessel was opened and washed with a cooled 1 *M*  $\text{H}_2\text{SO}_4$  solution in water of natural isotopic composition. Subsequently the  $\text{H}_2\text{O}_2^{18,18}$  was distilled off under vacuum together with most of the water ( $\text{H}_2\text{O}^{16}$ ). All other reagents were commercial chemicals of analytical grade. The pH values were determined by a Metrohm type E148C 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  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$ , and no "scrambling" between the oxygens of different molecules of  $\text{H}_2\text{O}_2$  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 $\text{H}_3\text{O}^+$ and

**OH<sup>-</sup>.**—The isotopic composition of H<sub>2</sub>O<sub>2</sub><sup>16,16</sup> in H<sub>2</sub>O<sup>18</sup> (92% O<sup>18</sup>) did not undergo any change in 1 *N* HClO<sub>4</sub> at 25° within 10 days. This result implies that the specific rate of exchange is smaller than 7 × 10<sup>-9</sup> min.<sup>-1</sup> at 25°.

In the alkaline range a 1 *N* NaOH solution of 0.1 *M* H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O<sup>18</sup> was kept at 25° for 11 days in a polyethylene vessel, 14% of the H<sub>2</sub>O<sub>2</sub> had decomposed during this period. The H<sub>2</sub>O<sub>2</sub> exchanged with the water (92% O<sup>18</sup>) at a specific rate of 1.1 × 10<sup>-7</sup> min.<sup>-1</sup>.

These results imply a half life of over 200 years for the spontaneous exchange of H<sub>2</sub>O<sub>2</sub> with water. On the other hand there is an indication for a nucleophilic substitution mechanism, which means that the OO bond of H<sub>2</sub>O<sub>2</sub> may eventually undergo an HO-OH polarization. This reaction is, however, an extremely slow process.

**2. Oxidation of H<sub>2</sub>O<sub>2</sub><sup>16,16</sup> in H<sub>2</sub>O<sup>18</sup> by Various Reagents and Catalysts.**—H<sub>2</sub>O<sub>2</sub><sup>16,16</sup> in enriched H<sub>2</sub>O<sup>18</sup> (92-94% O<sup>18</sup>) 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<sub>2</sub><sup>16,18</sup> in the evolved oxygen whereas an induced exchange from the solvent obviously increases it.

Several other reactants produced no induced exchange in the evolved O<sub>2</sub>: platinum black, lead dioxide, silver oxide, manganese dioxide, alkaline ferricyanide, bichromate in acid solution, bromine-bromide 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 O<sub>2</sub> 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 OCl<sup>-</sup> induced exchange in 0.2 *N* OH<sup>-</sup> solution at various concentrations of H<sub>2</sub>O<sub>2</sub> and OCl<sup>-</sup> and in presence of Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>2</sub><sup>-</sup> 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% O<sup>18</sup>. From the data it may be seen that the induced exchange in the oxygen evolved upon oxida-

TABLE I  
INDUCED EXCHANGE IN 0.2 *N* OH<sup>-</sup> SOLUTION OF H<sub>2</sub>O<sup>18</sup> (82% O<sup>18</sup>) BY HYPOCHLORITE IONS IN PRESENCE OF Cl<sup>-</sup>, Br<sup>-</sup> AND NO<sub>2</sub><sup>-</sup> IONS

(H <sub>2</sub> O <sub>2</sub> ) <sub>1</sub> , mole l. <sup>-1</sup>	(OCl <sup>-</sup> ) <sub>1</sub> , mole l. <sup>-1</sup>	Additive	(Addi- tive) mole l. <sup>-1</sup>	% O <sub>2</sub> <sup>16,18</sup> excess <sup>a</sup> in O <sub>2</sub> evolved	% H <sub>2</sub> O <sub>2</sub> <sup>16, 18</sup> excess <sup>a</sup> in H <sub>2</sub> O <sub>2</sub> residue
0.14	0.07	...	..	0.325	0.024
.14	.28	...	..	1.215	...
.28	.07	...	..	0.132	0.007
.028	.028	...	..	.559	.163 <sup>b</sup>
.14	.07	Cl <sup>-</sup>	0.1	.322	.022
.14	.07	Cl <sup>-</sup>	.5	.301	.021
.14	.07	Br <sup>-</sup>	.1	.058	.003
.14	.07	NO <sub>2</sub> <sup>-</sup>	.1	.040	.009
.14	.07	NO <sub>2</sub> <sup>-</sup>	.5	.022	Nil

<sup>a</sup> % O<sub>2</sub><sup>16,18</sup> excess =  $\frac{34/32 \times 100}{2 + 34/32} - 0.200$ . <sup>b</sup> Oxidation reaction stopped at 50% of completion.

tion of H<sub>2</sub>O<sub>2</sub> is higher than the exchange induced in the residual H<sub>2</sub>O<sub>2</sub>. The induced exchange both in the evolved oxygen and excess of OCl<sup>-</sup> 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<sup>-</sup> concentration from 5 to 0.5 molar.

In order to determine the source of the oxygen which appears in the evolved O<sub>2</sub> and in the H<sub>2</sub>O<sub>2</sub>, parallel runs were performed at 0.2 *N* OH<sup>-</sup> with OCl<sup>-</sup> of normal isotopic composition and with O<sup>18</sup>Cl<sup>-</sup> 90% enriched in O<sup>18</sup>. No oxygen exchange occurs at this alkalinity between OCl<sup>-</sup> and water.<sup>5</sup> No oxygen from the O<sup>18</sup>Cl<sup>-</sup> was detectable in the O<sub>2</sub> or in the residual H<sub>2</sub>O<sub>2</sub> when the reaction was carried out in H<sub>2</sub>O<sup>16</sup> and no difference in the isotopic composition of O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> was observed when H<sub>2</sub>O<sub>2</sub> in H<sub>2</sub>O<sup>16</sup> interacted either with O<sup>16</sup>Cl<sup>-</sup> or with O<sup>18</sup>Cl<sup>-</sup>.

It is suggested that HOCl which may be formed on H<sub>2</sub>O<sub>2</sub>-HOCl interaction as an intermediate<sup>6</sup> forms on hydrolysis hydrogen peroxide that may have exchanged with the solvent.



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.<sup>7</sup>

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 HOCl as intermediate.

**4. The Induced Exchange by Periodate and Permanganate Ions.**—The results of the interaction between H<sub>2</sub>O<sub>2</sub> and periodate in presence of chloride,

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

(6) R. E. Connick, *ibid.*, **69**, 1509 (1947); L. Erdey and J. Inczedy, *Acta Chim. Hung.*, **11**, 125 (1956).

(7) M. Anbar and S. Guttman, *J. Am. Chem. Soc.*, **83**, 2035 (1961).

TABLE II  
THE INDUCED EXCHANGE ON INTERACTION BETWEEN H<sub>2</sub>O<sub>2</sub>  
AND IO<sub>4</sub><sup>-</sup> AT pH = 7 IN 82% H<sub>2</sub>O<sup>18</sup> SOLUTIONS

(H <sub>2</sub> O <sub>2</sub> ) <sub>1</sub> , mole l. <sup>-1</sup>	(IO <sub>4</sub> <sup>-</sup> ) <sub>1</sub> , mole l. <sup>-1</sup>	Additive	(Addi- tive), mole l. <sup>-1</sup>	% O <sub>2</sub> <sup>16,18</sup> excess	% H <sub>2</sub> O <sub>2</sub> <sup>16,18</sup> excess
0.14	0.07	...	..	3.40	0.080
.48	.24	...	..	2.35	.022
.14	.14	...	..	3.22	.085 <sup>a</sup>
.07	.28	...	..	5.93	...
.14	.07	Cl <sup>-</sup>	0.1	1.64	0.045
.14	.07	Cl <sup>-</sup>	.5	0.39	0.027
.14	.07	Br <sup>-</sup>	.1	.075	Nil
.14	.07	Br <sup>-</sup>	.5	.012	Nil
.14	.07	NO <sub>2</sub> <sup>-</sup>	.1	.121	Nil
.14	.07	NO <sub>2</sub> <sup>-</sup>	.5	.063	Nil

<sup>a</sup> 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<sup>-</sup>, the induced exchange in the residual H<sub>2</sub>O<sub>2</sub> is smaller than that in the evolved O<sub>2</sub> and both decrease with H<sub>2</sub>O<sub>2</sub> concentration. Chloride, bromide and nitrite ions decrease this induced exchange considerably; the two last ions inhibit the induced exchange in the residual H<sub>2</sub>O<sub>2</sub> 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<sub>4</sub><sup>-</sup> and water is fast.<sup>8</sup> 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<sub>2</sub>IOOH but its formation seems rather likely and it may be of an analogous structure to that of O<sub>2</sub>NOOH.<sup>7</sup> The reactions of O<sub>2</sub>IOOH are unknown as well as their pH dependence, thus it is hard to give any interpretation to the pH 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<sub>2</sub>O<sub>2</sub> and water.

Nitrogen dioxide (200 mm.) was introduced into 0.2 N H<sub>2</sub>O<sub>2</sub><sup>16,16</sup> solutions in H<sub>2</sub>O<sup>18</sup> (82% O<sup>18</sup>) at pH = 12 and at pH = 6. After absorption of the gas, the residual H<sub>2</sub>O 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<sub>2</sub>O<sub>2</sub> yielded, besides a quantitative oxidation of the nitrite present, also an induced isotopic exchange in the residual H<sub>2</sub>O<sub>2</sub>. 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. Guttman, *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<sub>2</sub>NOOH<sup>-</sup> may be analogous to the formation of ONOOH which has been experimentally demonstrated.<sup>9</sup>

**6. The Induced Exchange by Ceric, Ferrous and Ferric Ions.**—The effects of Ce<sup>+4</sup>, Fe<sup>+3</sup> and Fe<sup>+2</sup> on the isotopic composition of the evolved O<sub>2</sub> and of the residual H<sub>2</sub>O<sub>2</sub> presented in Table III show trends similar to those of OCl<sup>-</sup>, IO<sub>4</sub><sup>-</sup> and MnO<sub>4</sub><sup>-</sup>.

TABLE III  
INDUCED EXCHANGE BY CERIC, FERRIC AND FERROUS IONS  
IN H<sub>2</sub>O<sup>18</sup> (80% O<sup>18</sup>)

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

The induced exchange increases at lower concentrations of the reagents and at lower relative concentrations of H<sub>2</sub>O<sub>2</sub>. 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<sub>2</sub>O<sub>2</sub> exceeds that in the evolved O<sub>2</sub>.

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<sup>++</sup>, FeOOH<sup>+</sup> and CeOOH<sup>+3</sup> are formed as intermediates. Complexes of this type have been postulated and even demonstrated spectrophotometrically<sup>10</sup>; thus the results may be considered as further evidence for their existence. It should be noted that FeOOH<sup>+</sup> does not yield oxygen on decomposition; this may be the reason that on decomposition of H<sub>2</sub>O<sub>2</sub> with Fe<sup>+2</sup> the induced exchange observed in the residual H<sub>2</sub>O<sub>2</sub> exceeds that of the evolved oxygen.

**7. Decomposition of Mixtures of H<sub>2</sub>O<sub>2</sub><sup>16,16</sup> and H<sub>2</sub>O<sub>2</sub><sup>18,18</sup> by Various Reagents.**—A series of reagents were examined for possible production of

(9) K. Gleu and R. Hubold, *Z. anorg. Chem.*, **223**, 305 (1935); M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6243 (1954).

(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).

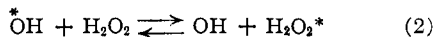
"scrambled" oxygen which originates from two different molecules of  $H_2O_2$ . They were also tested whether they induce an exchange between different molecules of hydrogen peroxide yielding "scrambled"  $H_2O_2$ <sup>16,18</sup>.

The first group of reagents tested were those which were found not to induce exchange and included: platinum black at  $pH = 1, 5$  and  $13$ ,  $PbO_2$ ,  $Ag_2O$  and  $MnO_2$  at  $pH = 5$ ;  $Fe(CN)_6^{-3}$  at  $pH = 13$ ;  $Cr_2O_7^{2-}$  in  $0.2 N H^+$ ;  $Br_2^- - Br^-$  and  $I_2 - I^-$  at  $pH = 4$  and  $HAuCl_4$  in  $0.5 N H^+$ . No scrambling could be detected within  $0.5\%$ , neither in the evolved gas nor in the residual  $H_2O_2$ . 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  $H_2O_2$  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  $MnO_4^-$  at  $0.5 N H^+$ ,  $Fe^{+3}$  and  $Fe^{+2}$  perchlorates at  $pH = 1.8$ ,  $Ce^{+4}$  in  $0.5 N H^+$ ,  $IO_4^-$  at  $pH = 3$  and  $pH = 9$  as well as  $OCl^-$  at  $pH = 13$  and finally nitrite at  $pH = 1$ ; in the last case only the residual  $H_2O_2$  was examined. All reagents of the second group with the exclusion of  $OCl^-$  showed zero scrambling both in  $O_2$  and in  $H_2O_2$  with  $1\%$  accuracy,  $OCl^-$  on the other hand showed  $4.2\%$  scrambling in the evolved gas and no scrambling in the residual  $H_2O_2$ .

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  $HO_2H$  and  $XOOH$ . The fact that no "scrambling" was observed in the ferri-ferro reactions<sup>11</sup> does not exclude the participation of OH radicals in these reactions; although some scrambling might be expected due to reaction 2 which was ob-



served in X ray irradiated systems,<sup>12</sup> the fast reaction of OH radicals with  $Fe^{++}$  might compete efficiently with the OH- $H_2O_2$  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

(11) R. C. Jarnegin and J. H. Wang, *J. Am. Chem. Soc.*, **80**, 786 (1958).

(12) M. Anbar, S. Guttman and G. Stein, *J. Chem. Phys.*, **34**, March (1961).

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.

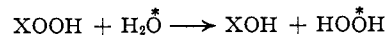
Following the similar behavior of the induced exchange by the various reactants, it may be concluded: (a) the extent of the exchange in the evolved oxygen is greater than that in the residual  $H_2O_2$ ; this would imply that the exchanged hydrogen peroxide is not the only precursor of the evolved oxygen; 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  $HO_2H$  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.<sup>7</sup> 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  $IO_2$  compared to Cl or  $Fe^{++}$ . The reactivity of  $XOOH$  toward reductants will follow a similar sequence, thus will  $O_2IOOH$  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:  $N_2O_4 + H_2O_2^{**} \rightarrow HNO_3 + O_2NOOH$ ;  $O_2NOOH + H_2O \rightleftharpoons O_2NOH + HOOH$ .

The isotopic exchange of oxygen between hydrogen peroxide and water was subject to a number of investigations<sup>1</sup> 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<sup>2</sup>  $k < 7 \times 10^{-9}$  at 25°.

A hydroxide ion catalyzed exchange was also observed<sup>3</sup> in 1 *N* NaOH with a rate constant of  $1.1 \times 10^{-7} \text{ min.}^{-1}$  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 XOOH, the O-O bond may be more vulnerable to a nucleophilic attack. Substituents having a strong negative inductive effect are for instance NO, Cl, NO<sub>2</sub> and SO<sub>3</sub>; the corresponding hydroperoxides ONOOH and ClOOH are only intermediates in hydroperoxide oxidation-reduction reactions.<sup>3,4</sup> O<sub>2</sub>NOOH-pernitric acid has been postulated in certain reactions,<sup>5</sup> persulfuric acid O<sub>3</sub>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<sub>2</sub>O<sub>2</sub>, but no quantitative conclusions could be derived owing to the transient nature of these hydroperoxides.<sup>2</sup> It was the purpose of this study to investigate the oxygen exchange between H<sub>2</sub>O<sub>2</sub> and water in a system where a stable hydroperoxide may be formed even if at low concentrations. Nitric or sulfuric acid solutions of H<sub>2</sub>O<sub>2</sub> may contain such stable hydroperoxides.

(1) E. R. S. Winter and A. V. A. Briscoe, *J. Am. Chem. Soc.*, **73**, 498 (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, Snee and Brasted, editors, D. Van Nostrand Co., New York, N. Y., 1956, p. 101.

### Experimental

H<sub>2</sub>O<sup>18</sup> 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<sub>2</sub>O<sub>2</sub> was determined gasometrically after catalytic decomposition over platinum black.

**Procedure.**—Solutions of H<sub>2</sub>O<sub>2</sub> in HNO<sub>3</sub> were placed in a thermostat at 60 ± 0.1° or at 100 ± 0.2°. Aliquots were taken at intervals and the H<sub>2</sub>O<sub>2</sub> was decomposed on a vacuum line over platinum black. It was found<sup>2</sup> that platinum black does not induce any exchange between H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> and analyzing the gas.

In experiments where the exchange reaction of nitrate ions was also followed, the nitrate was precipitated as Ba(NO<sub>3</sub>)<sub>2</sub> in an alcoholic solution. The dried Ba(NO<sub>3</sub>)<sub>2</sub> was heated with NH<sub>4</sub>Cl in excess in a sealed glass tube for 45 minutes at 400° to form N<sub>2</sub>O which was then analyzed.

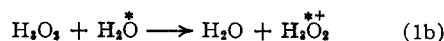
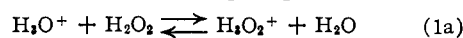
The mass spectrometric analysis was performed by a CEC model 21-401 Isotope Ratio Mass Spectrometer either by determining the ratio of masses 34/32 and 46/44 by the double collector or by determining the abundances of the individual masses.

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<sup>18</sup> 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 catalyzed mechanism for the exchange. Such a mechanism might involve reaction 1b as the rate determining step, reaction 1a being a fast pre-equilibrium.<sup>6</sup> Pre-



equilibrium 1a would require the specific rate con-

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