

CH₃ with NO; they favor a yield of 4.4×10^{-8} within one power of 10. Thus, for an assumed E_{16} near zero, they would favor a value of s_{16} not much greater than 10^{-4} . Lucas and Rice²⁶ studied photolysis of acetaldehyde by a rotating sector technique at a variety of temperatures and calculated the specific rate of the chain-breaking step. On the assumption that this step is reaction (16) they found $s_{16} \sim 1$ for $E_{16} \sim 0$, which latter value they favored, since k_{16} was found to be close to the estimated collision number of 10^{14} cc. mole⁻¹ sec.⁻¹ at 200°. Gomer and Kistiakowsky²⁷ made a similar study and concluded that the chain-ending step (contrary to Dodd²⁸) is reaction (16) and found $k_{16} = 4.5 \times 10^{13}$ cc. mole⁻¹ sec.⁻¹ at 125° and $E_{16} = 0 \pm 7$ kcal. We adopt the values $E_{16} \sim 0$ and $s_{16} \sim 1$. It has been shown⁴ that the values of E_1 and s_1 based on these latter values give reaction rates in reasonable agreement with those estimated by Rice⁵ from mirror experiments.

If E_{16} be taken equal to zero, work of Grahame and Rollefson²⁹ on high-temperature photolysis of acetaldehyde gives a value $E_{15} = 8.6$ kcal. This value has been re-examined by Dodd³⁰ with a rotating-sector technique. He concluded that $E_{15} =$

(26) V. E. Lucas and O. K. Rice, *J. Chem. Phys.*, **18**, 992 (1950).

(27) R. Gomer and G. B. Kistiakowsky, *ibid.*, **19**, 85 (1951).

(28) R. E. Dodd, *ibid.*, **18**, 234 (1950).

(29) D. C. Grahame and G. K. Rollefson, *ibid.*, **8**, 98 (1940).

(30) R. E. Dodd, *Trans. Faraday Soc.*, **47**, 56 (1951).

10.7 kcal. and that the earlier work was also consonant with that result.

Table V summarizes our conclusions regarding reactions (1) and (5). Low values of E_1 and E_5 are

TABLE V

CONCLUSIONS REGARDING ACTIVATION ENERGY AND STERIC FACTOR ON VARIOUS BASES

Base:	$E_{10} = 9.7^{21}$	$E_{15} = 8.6^{29}$	$E_{15} = 10.7^{30}$	$s_{16} = 10^{-4}$
Reaction (1)	13.2	13.7	15.8	10^{-2}
Reaction (2)	14.3	14.8	16.9	10^{-2}

based on the results of Trotman-Dickenson and Steacie²¹ on acetone and of Grahame and Rollefson²⁹ on acetaldehyde, respectively. They are in substantially good agreement. High values are based on the work of Dodd³⁰ on acetaldehyde. The photolysis of acetaldehyde is a chain reaction above 80° with a chain length of 300 at about 300°. Hence, no significant fraction of radicals present at any one time is suprathreshold and the acetaldehyde runs thus tend to be free from possible hot-radical effects. However, the difference between the values $E_1 = 13.2$ kcal. and $E_1 = 15.8$ kcal. are greater than we would expect on such a basis. Nevertheless, it may be said that $E_1 > 13$ kcal. and that $s_1 \sim 10^{-2}$.

(31) J. A. Leermakers, *THIS JOURNAL*, **56**, 1537 (1934).

NOTRE DAME, INDIANA

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(CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO)

The Use of Heavy Oxygen in the Study of Reactions of Hydrogen Peroxide¹

BY ALLEN E. CAHILL² AND HENRY TAUBE

In the oxidation of H₂O₂ in water solution by Ce(IV), MnO₄⁻, Cl₂, HClO, Cr₂O₇⁻, the O₂ formed is derived cleanly from the H₂O₂. The O₂ liberated in the decomposition of H₂O₂ by Fe(III), I⁻-I₂, Br⁻-Br₂, MnO₂ and Pt is also derived only from the H₂O₂. The isotope fractionation factors for the reduction of H₂O₂ by Ti(III), Fe(II), Sn(II), Cr(II) and Cu(I) at 25° are 0.994, 0.932, 0.943, <0.95, <0.945. The discrimination increases measurably when the temperature is lowered. For the reaction of the oxidizing agents Ce^{IV}, Cl₂, HOCl with H₂O₂, the factors are 0.987, 0.990 and 0.992, respectively. The fractionation factors characteristic of the oxidizing agent, and of the reducing agent which attack the molecules when Fe⁺⁺⁺, I⁻-I₂, Br⁻-Br₂ act catalytically have been determined. The slight discrimination exercised by Ti(III) in comparison with Fe(II), Sn(II), Cr(II) and Cu(I) has been interpreted as indicating a 1e⁻ reduction by it, but a 2e⁻ reduction of H₂O₂ by the other cationic reducing agents. The reducing intermediate present when Fe(III) acts catalytically has the same fractionation factor as Fe⁺⁺. It is concluded that the reducing intermediate is Fe(II) (and not HO₂). A mechanism for the catalysis of the decomposition of H₂O₂ and Fe(III) is proposed which incorporates this feature, and admits Fe(IV) as the usual product of the interaction of Fe(II) and H₂O₂. The 1e⁻ reduction of H₂O₂ by Fe(II) appears in the mechanism as a chain breaking step. Isotope fractionation by the heterogeneous catalysts MnO₂ and Pt was observed. The results to be expected for solids when diffusion limits the rate are outlined.

Significant information about the mechanisms by which hydrogen peroxide in water solution undergoes oxidation, reduction or catalytic decomposition can be gained by a study of the path of oxygen in these reactions. A number of investigations, with this as a goal have been carried out using O¹⁸ as a tracer.

Somewhat less obvious, but equally forceful in their implications as to mechanisms, are observations on the relative rates of reaction of oxidizing or reducing agents with isotopic species of hydrogen peroxide. The relative rate of reaction of a par-

ticular substance with isotopically distinct forms of another is a characteristic of the process, and has a value which varies only with temperature (or pressure). It can therefore be used to identify a particular process or reaction path, and to distinguish between processes. This application is particularly valuable in studying mechanisms by which catalysts act on hydrogen peroxide. The isotope fractionation exerted by catalysts can be analyzed into a fractionation factor for the production of oxygen, which is characteristic of the oxidation step in the catalysis, and the factor for the production of water, characteristic of the reducing agent present. The data are then useful in deciding whether the same intermediates act for different catalysts, and in comparing the unknown reducing

(1) The tracer work described in this paper was presented at the A.C.S. Meeting, Detroit, Mich., April, 1950; the results on fractionation in *New York*, Sept., 1951.

(2) A. E. C. Predoctoral Fellow, 1950-1951.

agents and oxidizing agents present during the catalytic process, with the effect of known substances. The fractionation factors are more convenient and less ambiguous in their implications than are kinetic data such as rates of reaction or activation energies. The latter quantities are usually composite in nature and include as factors contributions by steps generating the intermediates, destroying the intermediates as well as the steps of present interest: the attack of the hydrogen peroxide molecule by the active intermediates. The fractionation factors characteristic of the main path responsible for oxidation and/or reduction can conveniently be measured even for reactions with complex over-all mechanisms.

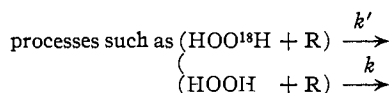
Experimental Methods

Definitions.—Symbols and definitions of frequent use in the presentation are as follows:

- f_o , the fractionation factor for oxidation of H_2O_2
 f_r , the fractionation factor for reduction of H_2O_2
 f_t , the fractionation factor for over-all reaction of H_2O_2 , without regard to distribution of isotopes within the products
 O_g, O_w, O_p , the number of oxygen atoms in the product gas O_2 , in the product water, and in the peroxide, respectively
 N , the mole fraction of O^{18} in the substance designated by the subscripts g, w or p as above. Right-hand superscripts will denote boundary fractional changes, 0 or 1
 x , the fraction of the hydrogen peroxide changed in a reaction. An asterisk will be used to denote a substance prepared enriched in O^{18} . The fractionation factors are defined by the equations

$$f_t = \frac{1}{N_p} \times \frac{dO_p^{18}}{dO_p}; f_o = \frac{1}{N_p} \times \frac{dO_g^{18}}{dO_g}; f_r = \frac{1}{N_p} \times \frac{dO_w^{18}}{dO_w}$$

The factors defined this way compare the rate of reaction of all species transferring O^{18} to products, with the total rate. To convert the values to comparisons of specific rates for



they must be corrected for the fact that the total rate includes reaction by O^{18} containing species, and that species such as $HO^{18}O^{18}H$ also transfer O^{18} to products. Since the level of enrichment is so small—2 parts per 1000—these corrections change the values of f inappreciably. Neglecting the contribution by doubly labeled H_2O_2 molecules it can be shown that

$$\frac{d(HO^{18}O^{18}H)}{d(HO^{18}O^{16}H)} \frac{(HO^{16}O^{18}H)}{(HO^{16}O^{16}H)} = \frac{k'}{k} = f_r \frac{(1 - 2N_p)}{(1 - 2f_r N_p)}$$

When $N_p = 2 \times 10^{-3}$ and f_r has the extreme value 0.93, the factor correcting f_r is 0.99972. It should be noted that the values of f as we have defined them will usually be less than 1.

The experiments were designed so that only oxygen was analyzed in the mass spectrometer. The isotopic composition of H_2O_2 was determined by measurements on the oxygen liberated by reaction with excess Ce^{IV} . The data of Table I show that there is no isotopic exchange with the environment in this process, and prove that the method gives an accurate assay of the isotopic composition of H_2O_2 . Oxygen exchanges among the forms H_2O_2 , H_2O and O_2 are sufficiently slow, so that the results are not affected thereby.

In the tracer oxidation experiments the isotopic composition of the hydrogen peroxide was compared with that of the oxygen liberated on complete oxidation in an O^{18} enriched environment. The tracer experiments on catalysis were done by comparing N_g^1/N_p^0 obtained for a normal environment with the ratio for an enriched environment.

The fractionation factors were measured by comparisons involving N_g and N_p . For reactions in which H_2O_2 is transformed completely to O_2 or to H_2O , the corresponding factors

f_o and f_r are equivalent to f_t . The relation of f_t to measurable quantities is

$$f_t = 1 + \frac{\log N_p/N_p^0}{\log(1-x)} \quad (1)$$

N_p^0 and N_p at some known fractional change x fix f_t . In the determinations of reduction factors, x varied from 0.6 to 0.95. In determining oxidation factors, it was found convenient to do this by comparing N_g for very small fractional decompositions ($x = 0.05$) with N_p^0 ($N_g/N_p \rightarrow f_o$ as $x \rightarrow 0$).

The catalytic decomposition can be construed as the simultaneous occurrence of oxidation and reduction of hydrogen peroxide. The sum and ratio of the corresponding factors f_o and f_r can be found as

$$f_t = \frac{1}{N_p} \frac{dO_g^{18} + dO_w^{18}}{dO_g + dO_w} = \frac{1}{N_p} \frac{(dO_g^{18} + dO_w^{18})}{2dO_g} = 1/2(f_o + f_r)$$

(note $dO_g = dO_w$ in catalytic decomposition)

$$f_o/f_r = \frac{dO_g^{18}}{dO_w^{18}} = \frac{O_g^{18}}{O_w^{18}} = \frac{xN_g}{2N_p - xN_g - 2N_p(1-x)} \quad (2)$$

When

$$x = 1, f_o/f_r = (N_g^1/2N_p^0 - N_g^1)$$

A convenient method of determining f_o and f_r is to apply the relation just preceding to the data at complete decomposition, and to obtain f_o as in the case of oxidizing agents, by comparing N_g with N_p^0 when x is small. It is interesting to note that the ratio N_g^1/N_p^0 does not depend on f_r and f_o separately, but on the ratio

$$N_g^1/N_p^0 = \frac{2f_o}{f_o + f_r} = \frac{2}{1 + f_r/f_o} \quad (3)$$

When $f_r = f_o$, $N_g^1/N_p^0 = 1$, whatever the absolute value of either. When $f_r < f_o$, $N_g^1/N_p^0 > 1$. This is the situation most often encountered.

All reactions producing O_2 were run by mixing solutions in an evacuated apparatus. The reductions were run in open vessels, but the reaction mixture was kept under an atmosphere of CO_2 for the experiments using readily auto-oxidizable reducing agents ($Cr(II)$, $Cu(I)$, $Ti(III)$). To obtain a sample of oxygen corresponding to small x , in the study of oxidizing agents, a deficiency of the reagent was used, and in the study of catalysts, the initial gas sample was removed as the reaction proceeded. All solutions were thoroughly outgassed before collecting samples of O_2 from them. The mass 28 (N_2) peak was measured for every sample and any result showing the presence of appreciable air in the sample, was rejected.

The H_2O_2 was Merck and Co., Inc., inhibitor free Superoxol. All salts were A.R. grade. A solution containing $Cr(ClO_4)_3$ was prepared by the method of Lingane and Pecsok³ and of $Mo(V)$ as described by Birnbaum and Walden.⁴ Ordinary distilled water was used except where otherwise noted. The buffer solutions of $pH \sim 7$ was prepared by dissolving 60 g. of KH_2PO_4 and 58 g. of K_2HPO_4 in 2 l. of water.

Isotope analyses except for a few early ones made by the Analytical Service of Consolidated Engineering Corp. were made on a Consolidated Nier Spectrometer, Model 21-201. The values of N measured in the later work, which includes all experiments except some of the tracer ones, are precise to $\pm 0.05\%$.

Results

Table I presents the results obtained in tracer studies on the oxidation of H_2O_2 .

The observations show that the oxygen liberated by MnO_4^- , Cl_2 , $HClO$ and $Cr_2O_7^{2-}$ on reaction with H_2O_2 in water is derived completely ($> 99.8\%$) from the H_2O_2 . The results obtained with $Ce(IV)$ are considerably more precise, and place an even smaller upper limit for admixture of oxygen from the solvent. $Ce(IV)$ is evidently a suitable oxidizing agent for isotopic assay of H_2O_2 , as is also MnO_4^- in acid solution.

(3) J. J. Lingane and R. L. Pecsok, *Anal. Chem.*, **20**, 425 (1940).

(4) N. Birnbaum and G. H. Walden, Jr., *This Journal*, **60**, 64 (1938).

TABLE I
TRACER RESULTS ON OXIDATION OF H₂O₂

No.	Oxidizing agent	$N_g^1/N_p^0 \times 10^3$ normal envir.	$N_g^1/N_p^0 \times 10^3$ 6-fold enriched
1	Ce(IV), H ⁺	2.018	2.018
2	MnO ₄ ⁻ , H ⁺	2.018	...
3 ^a	MnO ₄ ⁻ , ^b H ⁺	(2.014)	2.015
4	Cl ₂ , H ⁺ , Cl ⁻	2.014	2.013
5	HClO ^b (pH 7)	(2.014)	2.015
6	Cr ₂ O ₇ ⁻ , ^b H ⁺	(2.014)	2.015

^a Analyses for experiments 3-6 by Analytical Service Consolidated Engineering Corp. ^b Oxy-oxidizing agents in isotopic equilibrium with solvent. Values of N_g^1 for normal environment not determined, but set equal to value in Cl₂ experiment. In 3-6, same sample of H₂O₂ used.

The results of the tracer experiments with catalysts are reported in Table II.

TABLE II
TRACER RESULTS IN CATALYTIC DECOMPOSITION OF H₂O₂

Catalyst	N_g^1/N_p^0 normal envir.	N_g^1/N_p^0 6-fold enriched
Fe ⁺⁺⁺ , H ⁺	1.032	1.033
I ⁻ , I ₂ , pH ~ 7	1.017	1.014
Br ⁻ , Br ₂ , H ⁺	1.014	1.011
MnO ₂ , ^b H ⁺	1.005	1.010
Pt, H ⁺	...	1.002

^a Analyses performed here only for this experiment. ^b In isotopic equilibrium with the environment.

For most of the catalysts, N_g^1/N_p^0 is significantly in excess of 1.000. Since the ratio remains the same when the isotopic composition of the environment is changed, the effect is attributed to fractionation of the isotopes, rather than to transfer of solvent oxygen, or oxygen contained in the catalyst, to O₂. In no case is dilution by oxygen of the environment noted.

The data on the isotope fractionation exerted on H₂O₂ by various cationic reducing agents are presented in Tables III-VII.

TABLE III
FRACTIONATION IN Fe(II) REDUCTION

Ferrous salt	(Fe ⁺⁺)	(H ₂ SO ₄)	(H ₂ O ₂)	f_r	T, °C.
FeSO ₄ in all	0.10	7.0	1.0	0.932	25
experiments	.05	7.0	0.2	.934	25
	.04	5.0	.05	.930	4
	.02	5.0	.02	.931	5

TABLE IV
FRACTIONATION IN REDUCTION BY Sn(II)

Stannous salt	(Sn ⁺⁺)	(HCl)	(H ₂ O ₂)	f_r	T, °C.
SnCl ₂ in all	0.56	2.0	1.0	0.943	25
experiments	.25	3.0	0.2	.938	5
	.14	3.0	.1 ^a	.970	4

^a This solution was 0.1 M in Ti(SO₄)₂.

TABLE V
FRACTIONATION IN REDUCTION BY Ti(III)

Titanous salt	Salt concn.	(HCl)	(H ₂ O ₂)	f_r	T, °C.
TiCl ₃ in all	0.10	2.4	0.10	0.997	4
experiments	.02	2.4	.025	.998	4
	.02	2.4	.025 ^a	.998	5
	.04	3.0	.050 ^b	.994	4

^a This solution 0.5 M in NaF. ^b This solution 3.0 M in NaF.

The experiments sufficed to establish the values of f_r for Fe(II), Sn(II) and Ti(III), and for the former two ions at

TABLE VI
FRACTIONATION IN REDUCTION BY Cr(II)

Chromous salt	(Cr ⁺⁺)	(HClO ₄)	(H ₂ O ₂)	f_r	T, °C.
Cr(ClO ₄) ₂ in all	0.20	2.0	0.1	0.985	27
experiments	.09	2.0	.2	.981	27
	.04	2.0	.1	.971	26
	.02	2.0	.05	.965	26
	.10	2.0	.10	.976	5
	.012	2.0	.03	.950	5

TABLE VII
FRACTIONATION IN REDUCTION BY Cu(I)

Cuprous salt	Salt concentration	(HCl)	(H ₂ O ₂)	f_r	T, °C.
CuCl in all	0.04	2.4	0.2	0.948	26
experiments	.04	2.4	.1	.961	27
	.01	2.4	.02	.942	25
	.09	3.0	.10	.947	5
	.04	3.0	.10	.943	5

two different temperatures. It is evident that the differences between values of f_r for different reducing agents are great enough, so that they can be discriminated by measurements of precision ca. 0.1%. The experiments with Ti(III) are complicated by the formation of the Ti(IV)-H₂O₂ complex in the reaction. The formation of this complex, as judged by the color of the solution, was completely suppressed by the addition of 3 M NaF. The value of f_r to be compared with those of other reducing agents, is the value obtained in this experiment. Formation of the peroxy-complex raises f_r , as was shown also by adding Ti(IV) to a solution in which the reduction of H₂O₂ by Sn(II) was carried out.

With Cr(II) and Cu(I) as reducing agents, the values of f_r were found to depend on the rate of stirring, and on the ratio of concentration of reducing agent to H₂O₂. The lowest values were obtained at high stirring rates, and at low concentration ratios of reducing agent to oxidizing agents. The effect arises from the fact that Cr(II) and Cu(I) react very rapidly with H₂O₂ causing complete local reduction and yielding factors which are too high. The upper limit of f_r of 0.950 and 0.942 for Cr(II) and Cu(I), respectively, serve to show that the values for these cations are in the same range as those for Sn(II) and Fe(II).

Some experiments were also done with Mo(V) as reducing agent. The behavior of the system proved to be complex, and a meaningful comparison of the value of f_r for it, with those of other substances, cannot be made without a thorough study. In solutions of high acidity, 8 M or greater, Mo(V) is emerald green, but at lower acidity, 2 M or less, the color is amber. Although Mo(V) is a powerful reducing agent ($E^\circ = -0.56$)^b the reaction of the amber form with H₂O₂ is quite slow, and is complete only after several hours under conditions comparable to those used for the other reducing agents. The green solutions rapidly become amber when H₂O₂ is added, although the addition of a similar solution omitting H₂O₂ does not produce the color change. It is very likely that Mo(V) exists in solution in polynuclear forms, which would influence the reduction of H₂O₂ by it. A single measurement of f_r was made for an amber solution, yielding a value of 0.957.

The results obtained in the measurement of fractionation on oxidation are reported in Table VIII. The relatively high values of f_0 as compared to most of the values of f_r are consistent with the observations made for catalysts. Hydrolysis of Cl₂ is essentially complete at pH ~ 7, and the ex-

TABLE VIII
FRACTIONATION IN OXIDATIONS

Agent	(Agent)	(Acid)	(H ₂ O ₂)	f_0
Ce(HSO ₄) ₄	0.20	2.0	5.0	0.989
Cl ₂	.3 atm.	0.90	1.7	.990
Cl ₂	.1 atm.	pH 7	3.3	.992

(5) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc. New York, N. Y., 1938, p. 234.

TABLE IX

FRACTIONATION FACTORS IN THE DECOMPOSITION BY FERRIC SALTS								
Fe salt	T, °C.	Special conditions	Fe ⁺⁺⁺	HClO ₄	H ₂ O ₂	f _r	f ₀	
1 ^a Fe(ClO ₄) ₃	25	0.016	0.071	0.38	0.932	0.993	
2 Fe ₂ (SO ₄) ₃	2530	.30	.70	.932	.993	
3 Fe ₂ (SO ₄) ₃	2533	.11	1.0	.932	.993	
4 Fe ₂ (SO ₄) ₃	25	Redistilled H ₂ O	.60	.40	0.80	.933	.993	
5 Fe ₂ (SO ₄) ₃	25	Tap H ₂ O	.07	.08	.70	.932	.993	
6 Fe ₂ (SO ₄) ₃	25	H ₂ O, 6-fold enriched	.33	.11	1.0	.930	.993	
7 Fe ₂ (SO ₄) ₃	25	0.03 M EtOH	.33	.11	1.0	.935	.994	
8 Fe ₂ (SO ₄) ₃	25	.1 M EtOH	.10	.12	1.0	.935	.994	
9 Fe ₂ (SO ₄) ₃	010	.12	1.0	.929	.992	
10 Fe ₂ (SO ₄) ₃	0	0.03 M CH ₃ CHO	.10	.12	1.0	.936	.992	
11 Fe(ClO ₄) ₃	25	x = 0.36	.40	2.3	0.8	.939	.990	
12 Fe(ClO ₄) ₃	25	x = .36	.40	2.3	.8	.934	.993	
13 Fe(ClO ₄) ₃	25	x = .65	.040	0.19	.5	.915	.987	
14 Fe(ClO ₄) ₃	25	x = .65	.040	.19	.5	.934	.990	

^a Results are the mean of those obtained in 3 experiments which agreed within 0.05%.

periment therefore measures the fractionation for the reaction of HOCl and H₂O₂.

Of the catalysts, Fe(III) was studied most intensively. The results of the experiments on the decomposition of H₂O₂ catalyzed by ferric salts are shown in Table IX.

The data of Table IX lead to the conclusion that *f_r* for ferric salts at 25° is 0.932 and *f₀* is 0.993. The fractionation factors are independent of the concentration of Fe(III), H⁺ and H₂O₂, and are the same for ferric sulfate as for ferric perchlorate. They are not changed by liberal variations in the purity of the medium. This shows that the factors are characteristic of the ferric catalyst, and not of substances accidentally present. The fractionation factors for experiments 1-10 are based on isotope analyses of oxygen at *x* → 0 and *x* = 1, those for the last four experiments, by stopping the reaction at intermediate value of *x*. The results using the latter method are considerably less precise, owing to the difficulty of measuring *x* with sufficient precision and to complications introduced by the quenching procedure, which was to freeze the solutions. Comparisons of the mean with the results of the other experiments show, however, that the factors are substantially independent of *x*. Both *f₀* and *f_r* are decreased as the temperature is lowered. There is an increase in *f_r* when C₂H₅OH or CH₃CHO is added. No particular significance can be attached to these increases, since they may be the result merely of the net reduction of H₂O₂ by the organic substances which accompanies the catalytic decomposition. The values of *f₀* are independent of this circumstance and the increase observed when C₂H₅OH is added is due to a more subtle effect.

Experiments performed using Br⁻ and I⁻ as catalysts are reported in Table X.

TABLE X

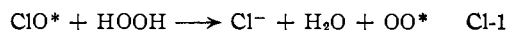
FRACTIONATION IN THE DECOMPOSITION BY I ⁻ AND Br ⁻					
Salt	Salt	H ⁺	H ₂ O ₂	f _r	f ₀
NaI	0.02	~10 ⁻⁷	1.0	0.945	0.976
NaI	.008	~10 ⁻⁷	1.0	.945	.976
NaI	.008	~10 ⁻⁷	1.0	.945	.976
NaBr	.10	0.09	0.80	.962	.988
NaBr	.20	0.19	1.0	.958	.985

The results on catalysis by Br⁻ are not accurate as to the actual values of *f₀* or *f_r*, although the ratio *f_r*/*f₀* is accurate. In the determination of *f₀*, *x* was not measured, but was calculated by substituting in equation 2 the value of *f₀*/*f_r* known from oxygen analysis on complete decomposition.

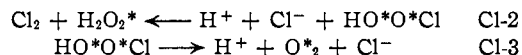
Discussion

The tracer experiments showed that when O₂ is liberated from H₂O₂ in water by a variety of oxidizing agents or catalysts, the O₂ is derived cleanly from H₂O₂, without noticeable admixture from H₂O or oxygen containing reagents. The observations exclude from consideration as mech-

anisms for reaction of oxy-oxidizing agents processes of the type illustrated for ClO⁻ as oxidizing agent



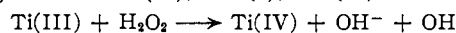
They are consistent with mechanisms of the type postulated⁶ for the reaction of Cl₂ and H₂O₂, in which a peroxy-complex of the oxidizing agent is formed (in this case HOOCI) which then undergoes electron rearrangement to form products.



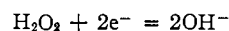
In view of the tracer experiments, it is unlikely that the oxygen-oxygen bond in peroxide is severed by any oxidizing agent. If oxidizing agents act primarily by removing electrons from the molecule, it is not expected that the O-O bond breaks on oxidation since removal of electrons from O₂⁻ strengthens the bond between the oxygen atoms.

The fractionation factors for reducing agents vary over a wide range, and the spread is sufficiently great so that the factors for various processes can be distinguished with measurements of precision 1 part per 1000. The factors observed on oxidation are closer to unity, and higher precision would be desirable in order to increase the power of this method of characterizing the reactions of oxidizing agents with H₂O₂.

The large difference between the fractionation factor for Ti(III) (0.994) and the factors for the other cationic reducing agent (~0.94) suggests a fundamental difference in mechanism of reduction. Of the cationic reducing agents, Ti(III) is the only one which on the basis of electron structure, is constrained to a 1e⁻ oxidation process. An interpretation of the difference in the magnitude of the values of *f_r* is that Ti(III) reduces H₂O₂ by a 1e⁻ change while Sn(II), Cu(I), Cr(II) and Fe(II)



act by 2e⁻ changes. In a 2e⁻ reduction of H₂O₂, it can reasonably be supposed that the O-O bond is completely severed in the activated complex

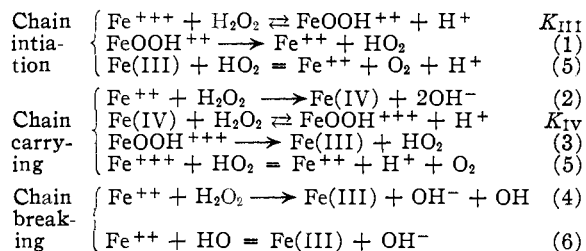


Since no vibration with respect to this coordinate is left in the activated complex, a maximum differ-

(6) R. E. Connick, THIS JOURNAL, 69, 1509 (1947).

and OH as the primary product on interaction of Fe^{++} and H_2O_2 .) A satisfactory mechanism should also be consistent with the observations on the Fe^{++} induced decomposition¹⁸ of H_2O_2 , and on other types of reaction of H_2O_2 induced by Fe^{++} .

A mechanism which describes the decomposition at high values of the ratio $(\text{H}_2\text{O}_2)/(\text{Fe(III)})$ is

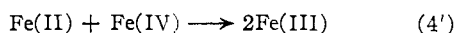


The rate law observed at high $(\text{H}_2\text{O}_2)/\text{Fe(III)}$

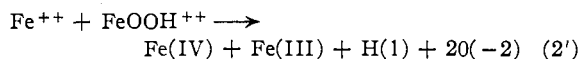
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k \frac{(\text{H}_2\text{O}_2)(\text{Fe}^{+++})}{(\text{H}^+)}$$

follows at once from the mechanism (if the chains are long) with $k = k_1 k_2 K_{\text{III}}/k_4$. It is assumed in the mechanism that Fe^{++} can attack H_2O_2 bivalently (reaction 2), continuing the chains, or monovalently (reaction 4) which breaks the chains, and that under the conditions prevailing, radicals such as HO_2 and HO are rapidly and efficiently spent by reaction with metal ions. The mechanism provides two paths for the decomposition of H_2O_2 , one based on the $\text{Fe(II)}-\text{Fe(IV)}$ couple (the chain carrying process) and the other based on the $\text{Fe(II)}-\text{Fe(III)}$ couple, incorporating the chain-initiating and chain-breaking steps. When the chains are long f_r will be determined by the chain carrying process; the measured value of f_r is therefore to be associated with reaction (2).

When Fe(III) is raised relative to H_2O_2 , the rate of production of oxygen is given¹⁶ by $k'(\text{Fe}^{+++})(\text{H}_2\text{O}_2)^{3/2}/(\text{H}^+)^n$ where n is greater than 1, but was not determined. At lower $(\text{H}_2\text{O}_2)/(\text{Fe(III)})$, Fe(IV) increases relative to H_2O_2 , and it is suggested that the chain breaking step



takes precedence over reaction 4. Further, when the ratio $(\text{FeOOH}^{++})/(\text{H}_2\text{O}_2)$ increases, it can be expected that the reaction of Fe^{++} with the ferric peroxide complex¹⁹



becomes important. Polarization of $-\text{O}-\text{OH}$ by Fe^{+++} can be expected to enhance the reactivity in the same way that polarization by HOSO_2^+ does (H_2SO_5 reacts much more rapidly with I^- than does H_2O_2). The mechanism modified by replacing reactions (4) and (2) by (4') and (2') leads to the rate law

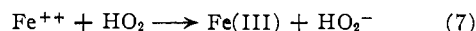
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k' \frac{(\text{Fe}^{+++})(\text{H}_2\text{O}_2)^{3/2}}{(\text{H}^+)^{3/2}}$$

In the reduction of H_2O_2 by Fe^{++} , the steady

(18) W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 461 (1951). References to earlier work are given in this article.

(19) M. G. Evans, P. George and N. Uri, *ibid.*, **45**, 230 (1949).

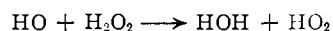
state concentration of Fe^{++} is high, and Fe^{++} competes efficiently with Fe(III) for reaction with HO_2 formed by reaction (3).



The relative rates of reactions (7) and (5) determine the extent of net reduction compared to the induced decomposition. The induced decomposition is increased by adding substances which oxidize HO_2 . This effect has been demonstrated¹⁸ for Fe(III) and Cu(II) .

There has been considerable interest in and discussion of the problem of the mechanism of attack of H_2O_2 by Fe^{++} , whether by a $1e^-$ change or $2e^-$ change. This paper makes an obvious restatement of the problem which is: Both mechanisms are possible and the problem is to determine the fraction of the change which goes by each path. It is proposed that the $2e^-$ change predominates under the conditions commonly studied. The ratio of the change by the $2e^-$ path compared to the $1e^-$ path will be given by the chain length in the ferric decomposition at high values $(\text{H}_2\text{O}_2)/(\text{Fe(III)})$. When peroxide is modified by replacing H by other groups, the ratio can change, and the $1e^-$ path may predominate. Similarly, for the reaction of Fe(IV) with H_2O_2 , a $2e^-$ path and a $1e^-$ path is possible. To make the mechanism for the Fe(III) catalysis compatible with the observations on the Fe^{++} induced decomposition, we have concluded that the $1e^-$ path predominates, although a share by the $2e^-$ path is not excluded.

An obvious gap in the work with Fe(III) is that the oxidation processes have not been sufficiently well characterized by the values of f_0 . Since the values are close to unity, substances of similar properties and mechanism (Cu(III) and Fe(IV) for example) might give values of f_0 not differentiated by the precision of our measurements. It seems certain, however, that careful work, extended to a variety of systems, can determine the value of f_0 for HO , and make it possible to decide more definitely whether this radical takes part as oxidizing agent in systems containing metal ions. Some experiments on the fractionation observed in the photochemical decomposition of H_2O_2 have been completed¹² but they have not given an unambiguous assignment of f_0 to the process.



The data of Table II give a rough measure of the fractionation on complete decomposition exerted by MnO_2 and Pt black. The results for solids may be influenced by diffusion to the surface. In this event, a diffusion fractionation factor f_d takes the place of f_t . The factor measured will not be simply f_d , but will be modified by the processes at the surface. When the reaction is diffusion controlled, f_0 and f_r cannot be separately determined, but a single factor characterizes the catalyst. This is easily seen for the case of $f_d = 1$. In this case H_2O_2 diffuses to the surface without isotope discrimination, and H_2O_2 reaching the surface is completely decomposed, the distribution of the isotopes among the products being determined by the ratio f_0/f_r . The essential difference between the case considered here and the homogeneous catalysis, is that here peroxide

reaching the catalyst either is oxidized or reduced while in the homogeneous case, the third choice of not reacting at all, is open.

The relationship for the diffusion controlled heterogeneous case can easily be seen using equation (3). The composition of H_2O_2 diffusing in at any time is $N_p f_d$. According to equation (3) this disproportionates as

$$\frac{N_g}{N_p f_d} = \frac{2}{1 + f_r/f_0}$$

whence N_g/N_p for the decomposition of an infinitesimal amount = $2 f_d/(1 + f_r/f_0)$. As $x \rightarrow 0$, $N_g/N_p \rightarrow 2f_d/(1 \times f_r/f_0)$. At complete decomposition, as the homogeneous case, $N_g/N_p = 2/(1 + f_r/f_0)$.

Measurements at both extremes permit f_d and f_r/f_0 to be determined.

The data we have obtained for solids are incomplete and are for complete decomposition. In view of the fact that f_0 for most substances is close to unity, it seems safe to conclude that for Pt, f_r is also close to unity, and that for MnO_2 , it is lower but still higher than for Fe^{++} or Sn^{++} .

Acknowledgment.—This research was supported by the Office of Naval Research under contract N6-ori-02026. The funds for the purchase of the mass spectrometer used in this research were supplied by the Atomic Energy Commission under contract AT(11-1)-92.

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The Kinetics of the Reaction of Thiosulfate Ion and Selenious Acid

By C. H. SORUM AND JOHN O. EDWARDS¹

The kinetics and mechanism of the oxidation of thiosulfate ion by hydrogen selenite ion have been investigated in the $p\text{H}$ range from 4.2 to 6.4 by means of the change in thiosulfate concentration and $p\text{H}$ with time. The reaction starts with the rate law, $-d[\text{S}_2\text{O}_3^{2-}]/dt = k_3[\text{HSeO}_3^-][\text{S}_2\text{O}_3^{2-}]^2[\text{H}^+]^2$. However, selenopentathionate ion is formed and this ion acts as a catalyst which greatly increases the reaction rate above $p\text{H}$ 4.5. The catalyzed reaction was found to have the rate law $-d[\text{S}_2\text{O}_3^{2-}]/dt = k_3[\text{HSeO}_3^-]^{1/2}[\text{S}_2\text{O}_3^{2-}]^{3/2}[\text{Se}(\text{S}_2\text{O}_3)_2^{2-}]^{1/2}[\text{H}^+]^{1/2}$. Some observations on the rate of formation of colloidal selenium showed that it is dependent to a large degree on the concentration of selenopentathionate and less so on the thiosulfate concentration. The rate of decomposition of selenopentathionate is greatly increased by sunlight.

Introduction

As part of a series of studies on the use of the $p\text{H}$ meter in the determination of reaction mechanisms, it was decided to investigate the oxidation of thiosulfate ion to tetrathionate ion by selenious acid. This reaction, which is essentially instantaneous in one normal acid, proceeds at a measurable speed above $p\text{H}$ 4. While the reaction kinetics are complex, and complete elucidation of the mechanism is not at hand, some of the results are clear-cut. These will be presented here.

When the concentration of thiosulfate ion is plotted as a function of time for the reaction be-

tween thiosulfate and hydrogen selenite ion at initial $p\text{H}$ values of 4.20, 4.94 and 5.10, curves 1, 2 and 3, respectively, of Fig. 1 are obtained. When the $p\text{H}$ of the reaction mixture is plotted as a function of time, curves 1, 2 and 3 of Fig. 2 are obtained for the same experiments as shown in Fig. 1. The similarity of number 1 curves in each figure, and of the number 2 curves, and of the number 3 curves, indicates that the $p\text{H}$ change complements the change in thiosulfate concentration. Hence the $p\text{H}$ change serves as an additional measure of the rate of the reaction despite the logarithmic nature of the $p\text{H}$ function.

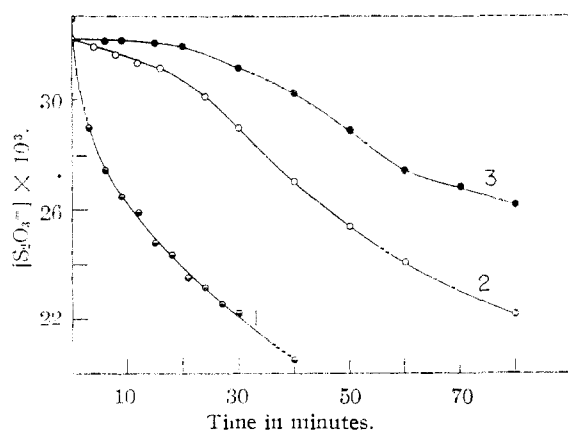


Fig. 1.—Change in thiosulfate ion concentration with time as a function of initial $p\text{H}$: $[\text{HSeO}_3^-] = [\text{S}_2\text{O}_3^{2-}]$; ionic strength = 0.210 ± 0.015 ; $t = 30.0^\circ$. Initial $p\text{H}$ values are 4.20, 4.94 and 5.10 for 1, 2 and 3, respectively.

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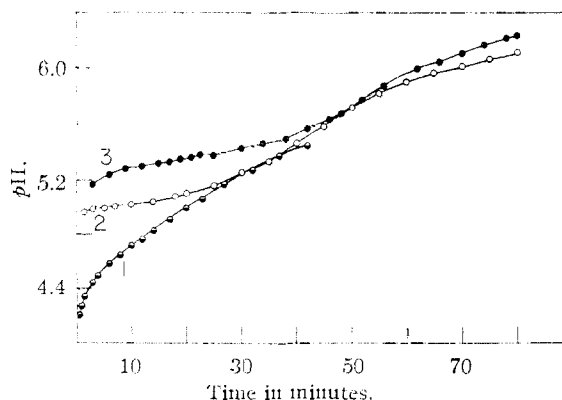


Fig. 2.—Change in $p\text{H}$ for the three experiments of Fig. 1.

The differences in the shapes of the curves in each figure demonstrate that the $p\text{H}$ of the system has a pronounced effect on both the rate and mechanism of the reaction. The upper half of curves 2 and 3 in Fig. 1 and the corresponding lower half of curves