Summary

A series of arylidine derivatives of N^4-acetyl-N^1-(4-amino)-phenylsulfanilamide and N^1-(4-amino)-phenylsulfanilamide have been prepared and their antibacterial efficacy against β-hemolytic streptococci and pneumococci will be reported elsewhere.

Kalamazoo, Michigan   Received September 9, 1940

[Contribution from the Chemical Laboratory of the University of California]

Chain Reactions in Aqueous Solutions Containing Ozone, Hydrogen Peroxide and Acid

By Henry Taube[1] and William C. Bray

In a continuation of the work of Rothmund and Burgstaller[1a,2] on the rate of interaction of ozone and hydrogen peroxide in acidic aqueous solutions, the two reactions that occur

$$H_2O_2 + O_3 = H_2O + 2O_2 \qquad (A)$$
$$2O_3 = 3O_2 \qquad (B)$$
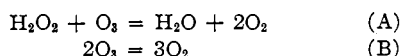
have been proved to be chain reactions. The effect of adding various inhibitors and catalysts has been investigated and the kinetics in the presence of one inhibitor, chloride ion, has been studied in detail. The only mechanism which we have found to correlate all the results of the present work requires the presence of the free radicals *hydroxyl* and *perhydroxyl* as intermediates in these homogeneous reactions.

A chain mechanism involving both these substances, HO and HO_2, has been suggested by a number of investigators to explain the decomposition of hydrogen peroxide solutions under various conditions, e. g., in the presence of enzymes,[3] at certain surfaces,[3] at metallic cathodes,[4] during the oxidation of ferrous ion[5] and in the presence of light.[6] It is to be noted that the decomposition occurs at surfaces in nearly all these instances, including the photodecomposition.[7]

Weiss[8] has advocated a similar mechanism for the OH^- catalyzed decomposition of ozone, and has used both mechanisms to explain the results of Rothmund and Burgstaller[1a]; but the experimental data are not extensive enough to prove or disprove chain mechanisms for these reactions.

Approximate values of the standard potentials of the various one and two electron couples in the oxygen system of compounds are presented below in the form used by Latimer[9] for other systems. Except in the case of the HO couples, these energy data are in agreement with the values selected by Latimer and by Bray.[2] The heat of dissociation of HO has now been decreased from about 116 kcal. to 104, a value which has been accepted by many investigators.[10]
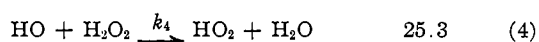
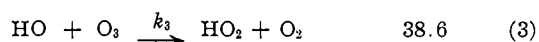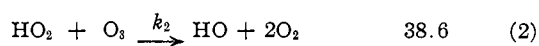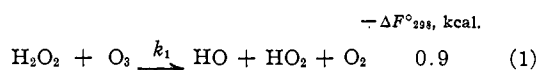Standard Potentials in Acid Solutions at $25°$
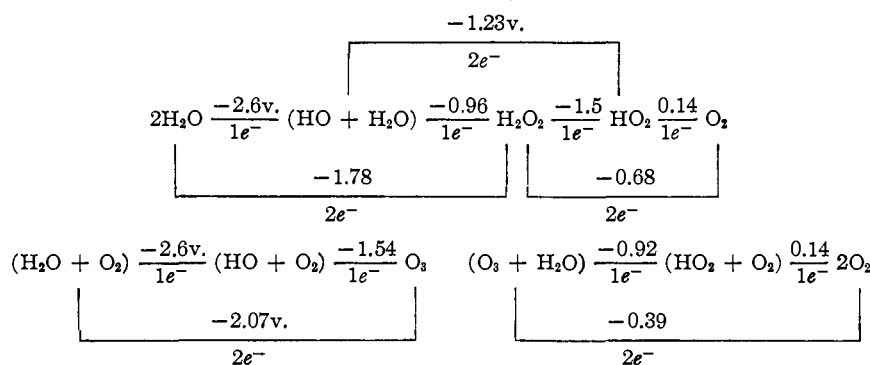
These charts show clearly the relation of HO and HO_2 to the better known oxidation states of oxygen, and facilitate the calculations of the standard free energy changes for reactions of these radicals.

(1) Abraham Rosenberg Research Fellow, 1939–40.
(1a) Rothmund and Burgstaller, *Monatsh.*, **38**, 295–303 (1917).
(2) Bray, This Journal, **60**, 82–87 (1938).
(3) Haber and Willstätter, *Ber.*, **64**, 2855 (1931).
(4) Weiss, *Trans. Faraday Soc.*, **31**, 1547–1557 (1934).
(5) Haber and Weiss, *Proc. Roy. Soc.* (London), **A147**, 332–351 (1934). A non-chain mechanism has been suggested by Bray and Gorin, This Journal, **54**, 2124–2125 (1932).
(6) Kornfeld, *Z. physik. Chem.*, **B29**, 205–214 (1935). This article contains references to earlier work on the photodecomposition.
(7) Rice, This Journal, **48**, 2106 (1926).

(8) Weiss, *Trans. Faraday Soc.*, **31**, 668–681 (1935).
(9) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.
(10) (a) Bonhoeffer and Reichert, *Z. physik. Chem.*, **A139**, 75–97 (1929); (b) Herzberg, *ibid.*, **B10**, 189–192 (1930); (c) Bates and Lavin, This Journal, **55**, 81 (1933); (d) Mecke, *Trans. Faraday Soc.*, **30**, 209 (1934).

To explain our experimental results it has been found necessary to assume the following intermediate reactions involving hydrogen peroxide, ozone and the two radicals:

$-\Delta F^{\circ}_{298}$, kcal.

$$H_2O_2 + O_3 \xrightarrow{k_1} HO + HO_2 + O_2 \quad 0.9 \quad (1)$$

$$HO_2 + O_3 \xrightarrow{k_2} HO + 2O_2 \quad 38.6 \quad (2)$$

$$HO + O_3 \xrightarrow{k_3} HO_2 + O_2 \quad 38.6 \quad (3)$$

$$HO + H_2O_2 \xrightarrow{k_4} HO_2 + H_2O \quad 25.3 \quad (4)$$

Reaction (1) is the chain-initiating step. Its actual free energy decrease will be large since the steady state concentrations of HO and HO₂ will be very small. The net result of (2) and (3) is the chain decomposition of ozone, reaction B. Similarly (2) and (4) constitute a chain process for reaction A.

Weiss[8] assumed these reactions and also

$$HO_2 + H_2O_2 \longrightarrow HO + H_2O + O_2$$
$$-\Delta F^{\circ}_{298} = 25.3 \text{ kcal.} \quad (4')$$
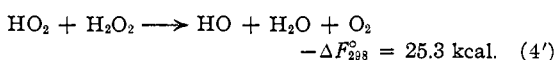
This reaction together with (4) would lead to a catalytic decomposition of hydrogen peroxide, and would require that in our solutions, as the ratio of peroxide to ozone is increased, the corresponding consumption ratio would exceed unity. However, Rothmund and Burgstaller[1a] established a limit of unity for this ratio, a result which we have checked. In the absence of ozone, a chain decomposition of hydrogen peroxide by reactions (4) and (4') may take place at surfaces, as in the photodecomposition.[6,7]

The present results on the action of inhibitors are consistent with the theory that the first step in the chain-breaking process is a $1e^-$-reaction of each inhibitor with HO, the most powerful and reactive oxidizing agent in the system.

$$HO + \text{Inhibitor} \xrightarrow{k_{5i}} \text{Radical} + HO_2 \quad (5i)$$
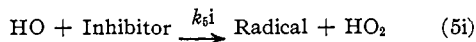
The conversion of the new radical into a stable product completes the chain breaking process. However, this radical, by taking part in another reaction, may also provide a new chain path for A or B.

Experimental Methods

The rates of the two reactions, A and B, that occur in an acidic aqueous solution of ozone and hydrogen peroxide have been determined at 0° and with varying concentrations of ozone, hydrogen peroxide, acid, inhibitors and catalysts. It was unnecessary to apply a correction for the

spontaneous decomposition of ozone; a $1.6 \times 10^{-3} M$ solution in 0.2 N HClO₄ lost only 5% of its oxidizing power in twenty hours, and this rate was found to be decreased by the inhibitors used. Bright daylight had no effect on the uninhibited reaction; its effect in the presence of inhibitors was not investigated.

In each experiment a solution of ozone was first prepared by bubbling ozonized oxygen through a solution of known acid concentration at a temperature of 0°. After the desired concentration had been reached a precooled solution containing hydrogen peroxide and any additional substance was added, and the mixture was shaken. Portions of the reaction mixture were drawn off into calibrated reaction cells, and placed in an ice-bath shielded from light. The cells were 100-cc. bulbs fitted with a narrow tube and ground glass stopper at the top, and with a stopcock and delivery tube at the bottom. They had a negligible gas space and could be emptied rapidly (in 5 sec. with applied air pressure). By their use a serious error due to the volatility of ozone was almost completely eliminated. Cells were withdrawn from the ice-bath at intervals and the reaction quenched by discharge below the surface of an acid bromide solution—the first step in the analysis for ozone and hydrogen peroxide. The first cell was quenched one or two minutes after the mixing of the reagents, and this time was taken as zero.

The method of analysis depends on the facts, first used by Rothmund and Burgstaller[1a,11] that ozone reacts rapidly with bromide ion over a wide range of H⁺ and Br⁻ concentrations

$$O_3 + 2H^+ + 2Br^- = O_2 + H_2O + Br_2,$$
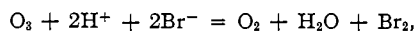
while hydrogen peroxide reacts very slowly with both bromide ion and bromine when the concentrations of H⁺ and Br⁻ are neither too high nor too low.[12] Accurate results were obtained by the following method: 50 cc. of an aqueous solution, 0.2 N sulfuric acid and 0.02 M sodium bromide, together with 75 cc. of carbon tetrachloride, was placed in a separatory funnel. The contents of a cell were introduced into the solution; the bromine liberated by the ozone was extracted with successive portions of carbon tetrachloride which had been freed from oxidizing and reducing agents, and determined iodimetrically. A three-way stopcock on the delivery tube of the funnel permitted the washing out of the delivery tube and thus minimized the loss of bromine. The hydrogen peroxide was left in the water layer and was determined iodimetrically; a small quantity of ammonium molybdate was used as a catalyst.

C. P. grades of perchloric, sulfuric and nitric acids were used. A large stock supply of perchloric acid was set aside, since different samples, in the absence of added inhibitor, gave different rates, presumably due to variation in their chloride content. Conductivity water was used as solvent. The hydrogen peroxide was Merck 30% superoxol, inhibitor free; it was checked against a sample prepared from sodium peroxide. The ozone was prepared by a standard method.[13]

(11) Rothmund and Burgstaller, *Monatsh.*, **34**, 693–704 (1913).
(12) Bray and Livingston, THIS JOURNAL, **45**, 1251–1271 (1923).
(13) Allmand and Spinks, *J. Chem. Soc.*, 1653 (1931).

The method of treating the data was similar to that used by Bray,[2] and is illustrated here by a typical example. The units are moles per liter and minutes. Parentheses denote concentrations. $P = (H_2O_2)(O_3)$.

$$k_A = \frac{\text{rate of A}}{P} = \frac{-d(H_2O_2)}{dt}/P =$$
$$-2.30\left(\frac{(d\log(H_2O_2)}{dt}\right)\left(\frac{1}{(O_3)}\right)$$

$$k_c = \frac{\text{rate of A} + \text{rate of B}}{P} = \frac{-d(O_3)}{dt}/P =$$
$$-2.30\left(\frac{d\log(O_3)}{dt}\right)\left(\frac{1}{(H_2O_2)}\right)$$

$$k_B = \frac{\text{rate of B}}{P} = k_c - k_A$$

In Fig. 1, log (O_3) and log (H_2O_2) for Expt. III (1) (Table III, Expt. (1)) are plotted against time. The slopes at definite times were determined by the use of a straight-edge, and the corresponding values of k_c and k_A calculated as indicated by the last terms in the above expressions for k_c and k_A.

Values, at the designated time, of (H_2O_2), (O_3), k_A, k_B, the consumption ratio, $R_c = (k_A + k_B)/k_A$, and the concentration ratio, $R_s = (H_2O_2)/(O_3)$, are given in Table I. The concentrations shown are those read from the smooth curves. Similar tables were prepared for all experiments[14] and intermediate values of k_A and k_B were determined by interpolation from these tables.

TABLE I

THE VARIATION OF THE SPECIFIC RATES AND THE CONSUMPTION RATIO DURING EXPT. III (1); cf. FIG. 1

Time, min.	(H_2O_2) × 10⁴	(O_3) × 10⁴	R_s	k_A	k_B	R_c
0	7.15	12.33	0.58	..	..	..
4	6.93	10.30	.67	7.1	55.7	8.84
12	6.56	7.36	.89	9.2	52.0	6.66
20	6.24	5.41	1.15	10.7	47.4	5.43
30	5.92	3.84	1.54	12.7	41.4	4.26
42	5.61	2.67	2.10	14.7	36.1	3.46
55	5.36	1.88	2.85	17.4	30.0	2.72
70	5.12	1.31	3.90	20.5	24.1	2.18

At high inhibitor concentration, a divergence as marked as that shown by one point in Fig. 1 was seldom noticed, and k_A and k_c in check experiments agreed within about 5%.

In general, neither k_A nor k_B is constant during a run. For any series of experiments considered in Sections I and II below the initial hydrogen peroxide and ozone concentrations were nearly constant. In Section III the changes in k_A and

(14) See Ph.D. thesis, Henry Taube, May, 1940, University of California Library.

k_B during experiments are used in establishing the rate laws of reactions A and B in the presence of the inhibitor, chloride ion.
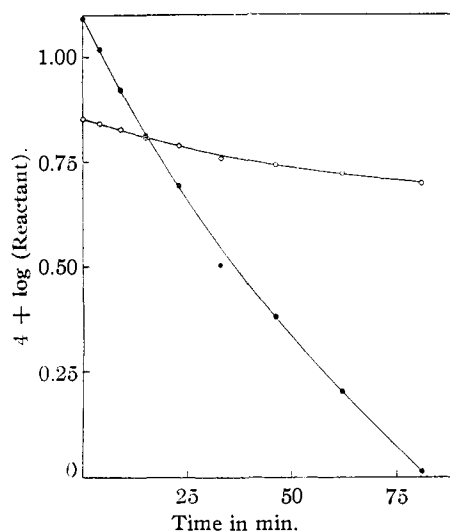

Fig. 1.—The decrease in the concentrations of ozone and hydrogen peroxide in a typical experiment. cf. Table I: ●, ozone; O, hydrogen peroxide.

I. Action of Inhibitors

The results of one series of experiments on the variation of k_A and k_B with the concentration of sodium chloride are presented in Table II, Expts. (1–10). The units and the definitions of the items tabulated have been given except for k_B', which is defined later in this section. In all the tables, the values of k_A and k_B shown for one experiment are correct only at the concentrations designated, and were obtained by interpolation from the complete table for the experiment.[14]

These results show the great sensitivity to the foreign material, chloride ion, of the reactions A and B and we conclude that they are chain reactions. Surface reactions also may be greatly inhibited by small amounts of foreign substance. It was shown, however, by a 5-fold variation in the ratio of surface to volume that the present reactions are not of this type in the absence of chloride ion, or with moderate amounts added.

The values of k_A in Expts. (9) to (12) were corrected for the slow oxidation of chloride ion by ozone. The corrections were based on the results of two experiments with mixtures of ozone and chloride ion in 0.19 M perchloric acid, which gave for the specific rate of the second order reaction the values 0.022 and 0.024. When hydrogen peroxide is also present the net result is a small con-

TABLE II

INHIBITION BY CHLORIDE ION IN 0.19 M HClO₄ AT 0°; *cf.* FIG. 4

No.	(Cl⁻) × 10⁴	$\frac{10^{-4}}{(Cl^-)}$	(H₂O₂) × 10⁴	(O₃) × 10⁴	R_a	k_A	k_B	R_o	k_B'
1	None		7.4	14.8	0.50	6.0	65.0	11.8	...
2	0.012	83.4	7.6	15.1	.50	4.0	42.0	11.5	118.0
3	.024	41.7	7.2	14.4	.50	3.6	27.5	8.6	48.0
4	.048	20.8	7.4	14.8	.50	3.2	16.1	6.0	21.0
5	.13	7.7	6.4	12.8	.50	2.4	8.7	4.63	10.2
6	.48	2.08	4.9	9.8	.50	1.7	2.8	2.65	2.88
7	1.00	1.00	6.7	14.8	.45	0.96	1.19	2.24	1.21
8	3.00	0.33	7.1	15.1	.47	.79	0.40	1.51	0.40
9	10.0	.10	7.2	16.0	.45	.58	.30	1.52	.30
10	50.0	.02	6.9	13.6	.50	.59	.26	1.44	.26
11	10.0	.10	21.6	6.9	3.13	1.10	.13	1.12	...
12	50.0	.02	22.9	6.2	3.70	0.92	.15	1.16	...

tribution to reaction A; experiments have shown that under these conditions chlorine and hypochlorous acid react rapidly with hydrogen peroxide, and that there is no induced decomposition of ozone. In Expt. (10) the correction was the greatest; 0.17 was subtracted from the experimental value to give the one tabulated.

The results of experiments to test several other substances as inhibitors are presented in Table III; Expt. II(7) is also included in this table as III(4).

TABLE III

INHIBITION OR CATALYSIS BY VARIOUS ADDED SUBSTANCES IN 0.19 M HClO₄

No.	Substance added	Concn. × 10⁴	(H₂O₂) × 10⁴	(O₃) × 10⁴	k_A	k_B
1	None	..	6.9	10.3	7.1	55.7
2	Formic acid	2	8.7	8.5	10.0	89.6
3	Sodium bromide	1	6.4	9.7	35.0	0.0
4	Sodium chloride	1	6.7	14.8	0.96	1.19
5	Propionic acid	2	9.4	12.5	.17	1.49
6	n-Amyl alcohol	2	9.8	13.2	Small	1.90
7	Methyl alcohol	2	10.0	11.0	Small	2.65
8	Ethyl alcohol	2	10.0	11.5	Small	3.00
9	Acetic acid	2	9.8	12.0	1.99	14.0

Inspection of the values of k_B shows that the substances designated in Expts. (3–9) are all good inhibitors for reaction B. The following substances, listed in order of decreasing efficiency, were shown by Richter[15] to inhibit the photodecomposition of hydrogen peroxide: n-hexanoic acid, amyl alcohol, ethyl alcohol, methyl alcohol, acetic acid. Anderson and Taylor[16] showed chloride and bromide ions to be inhibitors. Since the same types of substances are effective as inhibitors in both cases, and since the relative order of efficiency is nearly the same—the higher acids and

alcohols are more effective than the lower acids and alcohols and acetic acid is the least effective of the aliphatic series—it would seem almost certain that the same intermediate is involved in both reactions. The inhibition by chloride ion in our homogeneous reactions is particularly significant, since this shows the presence of a very powerful and reactive oxidizing agent, presumably HO, as an intermediate.

With the exception of bromide ion, the same substances markedly inhibit reaction A, Expts. III(3–9). In the case of the alcohols, the observed peroxide decrease was very small. In fact, with amyl alcohol there was a slight initial increase of the substance analyzed as peroxide, which indicates the formation of organic peroxides.

The effect of bromide ion deserves special attention. When this substance is mixed with a solution containing ozone, hydrogen peroxide and acid, there is an almost instantaneous reaction with ozone to give bromine. If the bromide ion is in excess the formation of bromine is the net result (and is the basis of the method of analysis). If the ozone is in excess, we observe a catalysis of reaction A, but inhibition of reaction B.

The catalytic action of formic acid will be discussed later.

On the basis of a simple mechanism involving only reactions (1), (2), (3), (4), (5i), and a reaction in which the new radical is converted into a stable product, it follows[17] that, as the inhibitor concentration is increased at nearly constant concentrations of ozone, peroxide, and hydrogen ion, k_B should vary inversely with the inhibitor concentration and should approach zero at the limit of

(15) Richter, *J. Chem. Soc.*, 1219–1224 (1934).

(16) Anderson and Taylor, THIS JOURNAL, **45**, 650–662, 1210–1217 (1923).

(17) (a) Bäckström, *ibid.*, **49**, 1460 (1927); (b) Alyea and Bäckström, *ibid.*, **51**, 91 (1929).

high inhibitor concentration; also k_A should vary in a similar manner, and in the limit should approach k_1, the specific rate of the chain-initiating step.

Data on the variation of k_A and k_B with the concentration of acetic acid[18] are presented in Table IV.

TABLE IV

INHIBITION BY ACETIC ACID IN 0.19 M HClO$_4$; $cf.$ FIGS. 2 AND 3

No.	(AcOH) × 10^4	$\frac{10^{-2}}{\text{(AcOH)}}$	(H$_2$O$_2$) × 10^4	(O$_3$) × 10^4	k_A	k_B	k_A'	k_B'
1	0	...	6.93	10.3	7.1	55.7	...	...
2	2	5.0	9.52	10.0	2.06	12.9	2.63	16.4
3	5	2.0	9.60	10.0	1.05	6.75	1.12	7.50
4	15(?)	0.67(?)	9.23	10.0	0.40	2.40	0.40	2.45
5	50	0.2	9.84	10.0	.20	1.38	.20	1.39
6	150	.067	9.52	10.0	.18	1.07	.18	1.07
7	300	.033	14.0	9.5	.14	0.57	...	...

In Fig. 2 a solid curve has been drawn through the values of k_B plotted against $1/(\text{AcOH})$. k_B was compared at 10^{-3} M O$_3$ since the variation of k_B during an experiment suggested that it depended mainly on this factor. The values of k_B', which are the values of k_B corrected[19] for any chain-breaking process other than that due to the added inhibitor, do fall on a straight line. However the limit for k_B at high inhibitor concentration is not zero, but has a value of 0.75.
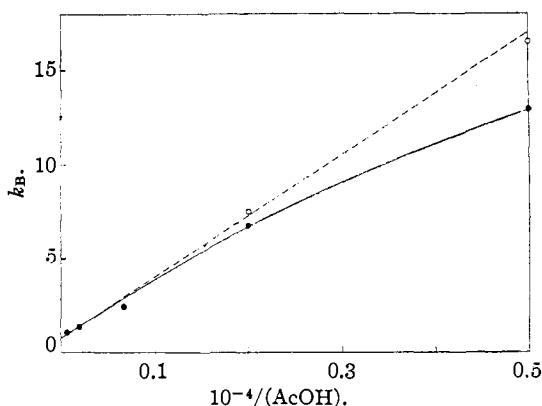

Fig. 2.—Variation of the specific rate of Reaction B with the reciprocal of the acetic acid concentration, $cf.$ Table IV: ●, k_B; O, k_B' (k_B corrected for the presence of other inhibitors).

The data for k_A in Table IV were treated in the same way, with the results shown in Fig. 3.

(18) Briner and Biedermann, $Helv.$ $Chim.$ $Acta$, **16**, 213 (1933), have shown that acetic acid does not react appreciably with ozone: hence it is suitable for this study.

(19) To make this correction when (AcOH) is the only variable we may use the relation ($cf.$ Ref. 17): $k(= k_B$ or $k_A) = k_l + p/[q(\text{AcOH} + 1]$. k_l is the limit which k reaches at high inhibitor concentration, $k_l + p$ is the value of k without added inhibitor. It follows that $k' = k_l + p/q(\text{AcOH}) = k_l + p(k - k_l)/[p - (k - k_l)]$. In calculating k_B', Table IV, the value $p = 54$ was used.
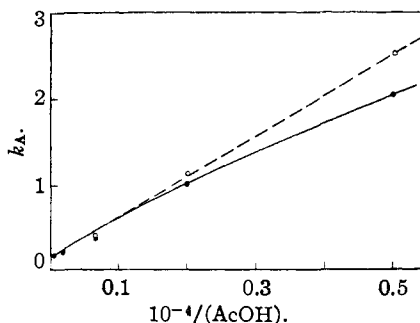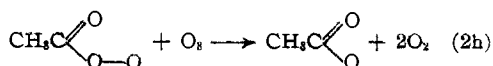

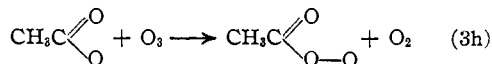Fig. 3.—Variation of k_A with $1/(\text{AcOH})$, $cf.$ Table IV: ●, k_A; O, k_A'.

Comparisons of k_A were made at $R_S = (\text{H}_2\text{O}_2)/(\text{O}_3) = 0.95$ and the values of k_A used were slightly different from those in the table. In calculating k_A', p was estimated to be 9.4 at this concentration ratio. Here again, the corrected specific rate varies inversely with the inhibitor concentration. The limiting value of k_A at high concentration of inhibitor is 0.13.

Expt. IV(7) was performed to determine whether the limits for k_A and k_B depend on the concentrations of the reactants. In this experiment the concentration of acetic acid is so high that in Figs. 2 and 3 the points would virtually lie at $1/(\text{AcOH}) = 0$. Comparing the values for $k_A = 0.14$ and $k_B = 0.57$ from this experiment with their respective limits obtained from Figs. 2 and 3, we can conclude that the limit for k_A is independent of the concentration of the reactants but that the limit for k_B does depend on this factor.

The fact that, at high concentration of the inhibitor, k_A approaches a definite limit shows that all the HO intermediate is used up by the acetic acid, and that the observed limit, 0.13, is the value of k_1, the specific rate of the reaction which produces HO and HO$_2$.

Since k_B does not approach zero in the limit, free radicals which react with ozone but not with hydrogen peroxide or acetic acid must be present. Such a limit is in general expected to vary with the concentrations of the reactants, as is observed in the present case. It is reasonable to suppose that reactions analogous to (2) and (3) take place, but that the acetate radical (CH$_3$COO) produced in the reaction of HO with acetic acid takes the place of HO while peracetate radical (CH$_3$COOO) takes the place of HO$_2$. The equations for the reactions are:

$$\text{CH}_3\text{C}\!\!\begin{array}{c}\nearrow\text{O}\\ \searrow\text{O}\!-\!\text{O}\end{array} + \text{O}_3 \longrightarrow \text{CH}_3\text{C}\!\!\begin{array}{c}\nearrow\text{O}\\ \searrow\text{O}\end{array} + 2\text{O}_2 \quad (2h)$$

$$CH_3C\underset{\diagdown O}{\overset{\diagup O}{}} + O_3 \longrightarrow CH_3C\underset{\diagdown O-O}{\overset{\diagup O}{}} + O_2 \quad (3h)$$

These two provide an additional chain process for reaction B.

Analysis of the reaction mixture showed that there was no noticeable formation of acetyl peroxide, peroxyacetic acid or carbon dioxide. Thus, acetic acid is probably regenerated. A chain terminating step which would accomplish this is

$$CH_3C\underset{\diagdown O}{\overset{\diagup O}{}} + CH_3C\underset{\diagdown O-O}{\overset{\diagup O}{}} + H_2O \longrightarrow 2CH_3COOH + O_2$$
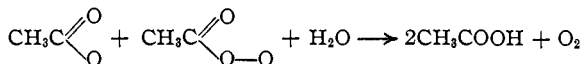
In Fig. 4, the data for k_B at high concentrations of chloride ion, Expts. II(4–10), are plotted against the reciprocal of the chloride ion concentration. The broken straight line is based on
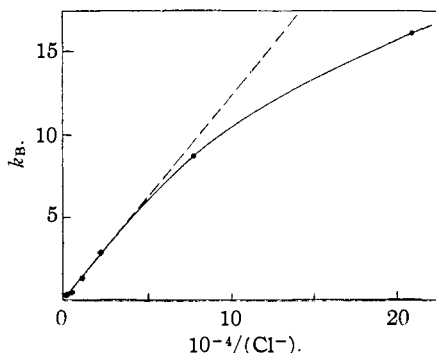

Fig. 4.—Variation of k_B with $1/(Cl^-)$, cf. Table II.

values of k_B' calculated[19] at smaller concentrations of chloride ion, using $p = 65$. There is a small but definite departure from linearity at the highest concentrations of chloride and the limiting value of k_B is about 0.25, not zero. When the data for k_A in the same experiments are treated in a similar manner, k_A' departs widely from a linear variation with $1/(Cl^-)$ and a high limiting value of k_A at high chloride is obtained, 0.55. Expts. (11) and (12) show that the limits for both k_B and k_A vary with the concentrations of peroxide and ozone. It may, therefore, be concluded that a new radical is produced (by the action of the inhibitor) which reacts with both ozone and peroxide to give additional chain processes. There is much evidence that this new radical is hydrated atomic chlorine, formed in the reaction

$$HO + H^+ + Cl^- = Cl + H_2O; \quad -\Delta F_{298}^\circ = 2.8 \text{ kcal.}[20]$$
$$(5)$$
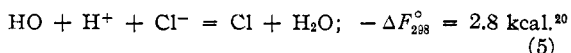
Atomic chlorine and ozone are known to react in

(20) The value of ΔF° for Cl gas given by Latimer[9] was used; cf. footnote 29.

the gas phase.[21] The reaction with hydrogen peroxide in solution

$$Cl + H_2O_2 = HO_2 + H^+ + Cl^-; \quad -\Delta F_{298}^\circ = 22.5 \text{ kcal.}$$
$$(6)$$
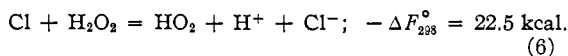
is analogous to that of atomic bromine, which has been shown to be a probable step in the photochemical chain reaction between hydrogen peroxide and bromine.[22]

Evidence that reaction (6) is important even at low concentrations of chloride ion is furnished by the marked decrease in the consumption ratio, R_c. If the chloride ion inhibitor operated merely by reacting with HO, without forming another radical reactive enough to take part in a new long chain, then R_c would have remained constant in the region of long chain lengths. Referring to Table II, we observe that at $4.8 \times 10^{-6} M$ Cl^-, R_c has decreased to one-half the value it had in the blank experiment, although k_A is still five or six times its limit at high chloride. The original HO radical is being replaced (owing to its reaction with chloride ion) by another which is capable of taking part in a new long chain involving hydrogen peroxide and with reaction A as the net result.

It seems worth while to point out that the experimental requirements are not fulfilled if HO_2 rather than HO is assumed to react with chloride ion to form a new radical. This assumption would require that, at high ratio of hydrogen peroxide to ozone and high chloride concentration, the consumption ratio, R_c, becomes less than the observed limit of unity, since the proportion of the HO and of the new radical that react with hydrogen peroxide rather than with ozone would continue to increase as the peroxide–ozone ratio becomes greater.

Fluoride ion at a concentration of $2.5 \times 10^{-5} M$ does not affect reaction A or B in 0.19 M perchloric acid. This result was to be expected, since HO is not able to oxidize fluoride ion to atomic fluorine; the standard potential for the $F^-_{aq.} - F_{gas}$ couple is -4.04 v.

Iodide ion at $10^{-5} M$ also does not have any effect; it seems likely that the ozone rapidly oxidizes the iodide to iodate ion, which, under the conditions of the experiments, is not reduced rapidly by hydrogen peroxide; hence the substance is in effect removed from the system.

(21) Rollefson and Burton, "Photochemistry," Prentice-Hall, Inc., New York, N. Y., 1939, pp. 286–288.

(22) Callow, Griffith and McKeown, Trans. Faraday Soc., 35, 412–420 (1939).

Some experiments were performed to gain an insight into the chain-breaking processes which obtain in the absence of added inhibitors, although the sensitivity to traces of impurities makes an exact kinetic study difficult.

In one series of experiments with small concentrations of ozone in 0.19 M $HClO_4$ and with increasing concentrations of peroxide, k_B was found to decrease to zero and k_A to increase to a limiting value of 25 to 30.[23] The value of k_B and the limit for k_A were found to decrease with increasing concentration of perchlorate ion and of hydrogen ion. This result indicates that even perchloric acid acts as inhibitor.

Table V shows a comparison of the rates of A and B in perchloric, nitric, and sulfuric acid solutions. The chloride contents of the solutions calculated from the maximum chloride content stated on the labels are 20, 1.5, and 2×10^{-7} M, respectively. Comparison of Expts. (1) and (3) shows the discrepancy in samples of perchloric acid from two different shipments. The acid in Expt. (1) was older, and Cl^- was probably formed by a photochemical decomposition prior to its

TABLE V

COMPARISON OF THE SPECIFIC RATES IN PERCHLORIC, NITRIC AND SULFURIC ACID SOLUTIONS

No.	Acid	(H_2O_2) $\times 10^4$	(O_3) $\times 10^4$	R_s	k_A	k_B	R_c
1	0.19 M $HClO_4$	6.9	10.9	0.63	7.8	55	8.1
2	.21 M HNO_3	7.5	11.9	.63	18.0	36	3.0
3	.21 M $HClO_4$	9.8	8.8	1.1	18	88	5.9
4	.17 M H_2SO_4	9.7	8.7	1.1	24	58	3.4

use. It seems certain, therefore, that the nitric acid solution, Expt. (2) had less chloride in it than the perchloric acid in Expt. (1), and we must conclude that the lower value of k_B in the nitric acid experiment is a result of the inhibitory action of NO_3^-. A similar observation can be made for SO_4^{--}, by comparing (3) and (4).

The R_c values show that the inhibitory action of SO_4^{--} or NO_3^- is much less for reaction A than for B; in fact, catalysis of A by NO_3^-, as compared with ClO_4^-, may be noted. The variable values of R_c in these cases require the operation of new radicals which have a higher probability of reaction with peroxide in the nitric acid system than in the perchlorate. The simplest interpretation seems to be that hydroxyl oxidizes the anions ClO_4^-, SO_4^{--} or HSO_4^- and NO_3^- to the

(23) A similar behavior of k_B and k_A was noted by Bray[2] in Rothmund and Burgstaller's experiments in 0.01 N H_2SO_4: the limiting value of k_A was 35 to 50.

corresponding radicals. These may react with peroxide by reactions analogous to (6), thus causing R_c to vary; or may disappear in a chain-breaking step, e. g. by reaction with HO_2. The preparation of substances of the composition NO_3[24] and ClO_4[25] has been claimed, but we have found no definite evidence of the existence of radicals with structures corresponding to the ions. SO_4^- has been shown by a kinetic investigation to be a possible intermediate in the reaction between $S_2O_8^{--}$ and $Fe(CN)_6^{-4}$ ions.[26]

II. Catalysis

In Table VI data are presented which illustrate the effect of various positive ions on reactions A and B. R_c' represents the consumption ratio, $R_c = (k_A + k_B)/k_A$, estimated from the blank experiment, at the concentration ratio, R_s, obtaining in a particular experiment.

TABLE VI

EFFECT OF VARIOUS POSITIVE IONS ON REACTIONS A AND B IN 0.19 M $HClO_4$

No.	Subst. added	(M^{+n}) $\times 10^5$	(H_2O_2) $\times 10^4$	(O_3) $\times 10^4$	k_A	k_B	R_c	R_c'
1	None	..	6.56	7.36	9.2	52.0	6.7	..
2	$NiSO_4$	2.5	6.93	10.72	7.1	57.5	9.1	9.7
3	$Pb(NO_3)_2$	2.5	6.71	11.30	6.9	49.1	8.2	11.7
4	$La_2(SO_3)_4$	2.5	6.69	8.95	9.2	55.0	7.0	7.9
5	$Nd_2(SO_4)_3$	2.5	6.87	9.44	8.1	49.2	7.1	8.3
6	$FeSO_4$	2.5	6.59	8.17	7.3	56.1	8.7	7.7
7	$Cr_2(SO_4)_3$	2.5	6.68	10.30	6.8	56.5	9.3	9.7
8	$CoSO_4$	2.5	6.35	8.65	18.8	136	8.2	8.3
9	$Ce_2(SO_4)_3$	3.9	6.07	6.31	47.2	273	6.8	6.3
10	$Ce(SO_4)_2$	5.0	5.37	4.96	87.0	389	5.5	5.9
11	Ag_2SO_4	2.5	5.07	11.30	49.0	75	2.5	13.3
12	Tl_2SO_4	2.5	6.56	9.33	29.1	208	8.2	8.9
13	$CuSO_4$	3.3	5.11	9.72	9.8	104	11.6	11.5
14	$CuSO_4$	10.0	4.93	9.87	10.6	110	11.4	12.0
15	None	..	4.77	10.80	4.6	51	12.2	..

Comparing the values of k_B with that in the corresponding blank experiment—Expt. (1) is the blank for (2–12); Expt. (15) is the blank for (13) and (14)—we observe that the ions Co^{++}, Ce^{+3}, Ce^{+4}, Ag^+, Tl^+ and Cu^{++} markedly accelerate the decomposition of ozone. If allowance is made for the concentration differences in the Ce^{+3} and Ce^{+4} experiments, the two ions have about the same effect. In Table X it is shown that Pr^{+3} also has a catalytic effect. The ions Ni^{++}, Pb^{++}, La^{+3}, Nd^{+3}, Fe^{++} and Cr^{+3} are without such an effect, within the limits of the experimental error.

The group which has marked catalytic effect consists of oxidation–reduction couples with the

(24) See the critical discussion of Klemenc and Neumann, Z. anorg. allgem. Chem., 232, 216–224 (1937).

(25) Gomberg, THIS JOURNAL, 45, 398–421 (1923).

(26) Holluta and Herrmann, Z. physik. Chem., A166, 453–467 (1933).

following characteristics: the reducing agent can be oxidized by a $1e^-$ change, and the oxidizing agent can be reduced rapidly by hydrogen peroxide. The oxidation states Tl^{++}, Cu^{+3}, Pr^{+4} are unstable at any appreciable concentration, but there is good evidence for their existence.[27] Ag^{++} is now a well-known oxidation state of silver.[28] Any member of the non-catalytic class fails to fulfill one or other of these requirements. For example, although Fe^{++} can be oxidized by a $1e^-$ process, Fe^{+3} is not reduced rapidly by hydrogen peroxide.

With the exception of Ag^+, the catalysts affect reactions A and B to about the same extent, as can be seen by comparing the consumption ratios, R_c, with those, R_c', estimated from the blank. Ag^+ catalyzes reaction A much more than it catalyzes reaction B.

In the non-catalytic group the decreased consumption ratio observed with lead nitrate can be attributed to the presence of nitrate ion, which in the previous section was shown to give such an effect.

The properties characteristic of the catalysts considered above suggest that they react in this system as follows

$$M^{+n} + H^+ + O_3 = M^{+n+1} + HO + O_2 \quad (1a)$$
$$M^{+n+1} + H_2O_2 = M^{+n} + HO_2 + H^+ \quad (1b)$$
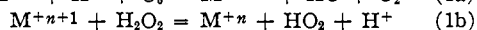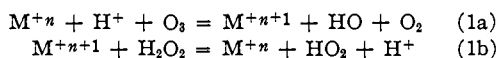
The net effect of the two reactions is an increase in the steady state concentrations of the free radicals, due to the enhanced rate of production.

Both reactions can be subjected to experimental test. Reaction (1a) predicts that, in a mixture of Ce^{+3} and ozone, the ozone should undergo a catalytic decomposition, since the HO will start a chain decomposition by reactions (2) and (3).

Some of the results of such experiments are contained in Table VII. These experiments were done in sulfuric acid solution but similar effects would have been observed in perchloric acid solutions; the results in Tables IX and X show that in sulfuric acid catalytic effects were observed with some of the ions used in the perchloric acid experiments, Table VI.

The figures in column 6 represent the ratio of the decrease in the ozone concentration to the initial concentration of the added metal ion. It is apparent from these figures that a considerable

(27) Mellor, "Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1923.
(28) Noyes, DeVault, Coryell and Deahl, THIS JOURNAL, **59**, 1326 (1937).

TABLE VII

EFFECT OF CERTAIN METAL IONS ON THE DECOMPOSITION OF OZONE IN 0.1 M H_2SO_4

No.	Subst. added	(M^{+n}) $\times 10^5$	Time, min.	(O_3) $\times 10^4$	$\dfrac{\Delta(O_3)}{(M^{+n} \text{ added})}$	$-d(O_3)/dt$ $\times 10^7$
1	$CoSO_4$	4	10	12.40		12.9
			280	9.67	7.1	7.6
2	$CoSO_4$	7	20	12.33		22.1
			190	9.33	4.91	14.1
3	$Ce_2(SO_4)_3$	4	5	12.47		66.4
			400	10.47	6.1	Small
4	$CuSO_4$	66	1800	12.10	(6% decomposed)	

amount of ozone is decomposed, in addition to that consumed in the oxidation of the metal ion. Column 7 gives the actual rates of disappearance of ozone, determined from plots (for all the data) of log (O_3) against time. In the cerous ion experiment this rate drops to zero after about 400 minutes, presumably due to complete oxidation of cerous ion by the ozone in that interval of time. We may therefore conclude that the excess decomposition of ozone observed in these experiments results not from a catalysis by Ce^{+4} or Co^{+3}, but is induced by the oxidation of Ce^{+3} and Co^{++}. This is the result predicted by assuming reaction 1(a) as the first step in the interaction of Ce^{+3} or Co^{++} with ozone.

The rate of decomposition of ozone in the presence of copper ion is of the order of that observed for ozone alone in acid solution. Thus, we cannot explain the copper ion catalysis, Table VI, by reactions (1a) and (1b).

Reaction (1b) was subjected to a similar experimental test. This reaction predicts that, when a mixture of Ce^{+4} and ozone is added to hydrogen peroxide, the (very rapid) reaction between Ce^{+4} and peroxide should induce a decomposition of ozone by reactions (2) and (3); that is, in addition to an instantaneous decrease in the peroxide and ceric ion concentrations, a large decrease in the ozone concentration should be observed. The data are presented in Table VIII. The solutions were analyzed immediately

TABLE VIII

DECOMPOSITION OF OZONE INDUCED BY THE REACTION BETWEEN HYDROGEN PEROXIDE AND CERIC ION IN 0.1 M H_2SO_4

No.	(Cl^-)	Subst.	Initial	Final	Δ = decrease
				Concentration $\times 10^4$	
1	None added	O_3	11.54	3.87	7.67
		Ce^{+4}	4.69	0.0	4.69
		H_2O_2	7.70	3.17	4.53
2	$10^{-2} M$	O_3	7.83	6.26	1.57
		Ce^{+4}	4.44	0.0	4.44
		H_2O_2	7.60	3.84	3.76

after mixing and the reaction time was of the order of 0.25 to 0.5 minute.

We observe in the first experiment a large instantaneous decrease in the concentration of ozone, much more than would be found in the same interval with a mixture of cerous ion, hydrogen peroxide and ozone. Thus we conclude that a decomposition of ozone is induced by the reaction between peroxide and ceric ion.

Expt. VIII(2) shows that the addition of chloride ion decreases the catalytic decomposition. The hydrogen peroxide consumed is very nearly equal to that required to react quantitatively with the ozone and the ceric ion; thus reaction B is almost entirely eliminated at 10^{-2} M Cl$^-$. This result is predicted by an HO, HO$_2$ mechanism for this reaction.

If the only function of the metal ions is to increase the rate of production of free radicals by reactions (1a) and (1b), k_A and k_B will increase linearly with increasing metal ion concentration, and R_c will remain constant.

Tables IX and X contain data on the variation of k_A and k_B with metal ion concentration. The constants have been compared at R_s = 0.325. The variation of k_A and k_B due to slight differences in the initial concentrations will not affect

the conclusions to be drawn. The values of k_A and k_B in the blank experiment, IX(1), are not inconsistent with those obtained in Expt. V(4) under other conditions.

In Expts. IX(2–5) both specific rates increase with increasing concentration of the catalyst, but the consumption ratio, R_c, decreases.

Expts. X(2–7) show that Pr^{+3} and Cu^{++} are effective catalysts in the presence of chloride ion at a concentration high enough to lower k_B to about half its value; cf. Expts. IX(1) and X(1). The specific rates are less in Expt. X(5) than in the corresponding experiment without added chloride, IX(6). R_c is nearly constant in the praseodymium experiments but decreases as the concentration of copper ion is increased.

In Fig. 5 the values of k_B in the Co^{++}, Pr^{+3} and Cu^{++} experiments are plotted against the concentration of metal ion. Each of the ions gives a sharp initial rise. With Co^{++} and Pr^{+3}, this changes to a less rapid, nearly linear rise; but, with Cu^{++}, k_B levels off to a constant value. Expts. VI(13–15) show a similar behavior with Cu^{++} in perchloric acid solution.

TABLE IX

EFFECT OF VARYING THE CONCENTRATION OF COBALTOUS ION IN 0.1 M H$_2$SO$_4$; cf. FIG. 5

No.	Subst. added	(M^{+n}) $\times 10^5$	(H_2O_2) $\times 10^4$	(O_3) $\times 10^4$	k_A	k_B	R_c
1	None	..	3.35	10.30	30	148	6.21
2	CoSO$_4$	1.3	2.70	8.32	41	214	6.24
3	CoSO$_4$	4.0	2.72	8.38	50	248	5.95
4	CoSO$_4$	6.6	2.30	7.08	68	279	5.10
5	CoSO$_4$	33.0	2.60	8.00	130	470	4.60
6	CuSO$_4$	3.3	2.80	8.61	41	219	6.37

TABLE X

EFFECT OF VARYING CATALYST CONCENTRATION IN THE PRESENCE OF 3×10^{-7} M CHLORIDE ION IN 0.1 M H$_2$SO$_4$; cf. FIG. 5

No.	Catalyst added	(M^{+n}) $\times 10^5$	(H_2O_2) $\times 10^4$	(O_3) $\times 10^4$	k_A	k_B	R_c
1	None	..	3.11	9.56	10.4	66	7.5
2	Pr$_2$(SO$_4$)$_3$	1.0	3.28	10.10	18	117	7.4
3	Pr$_2$(SO$_4$)$_3$	2.5	3.52	10.92	25	143	7.1
4	Pr$_2$(SO$_4$)$_3$	10.0	3.02	9.28	48	325	7.8
5	CuSO$_4$	3.3	3.28	10.10	19[a]	151	7.9[b]
6	CuSO$_4$	10.0	2.57	7.94	28[a]	176	7.0[b]
7	CuSO$_4$	66.0	2.32	7.14	37[a]	173	5.9[b]

[a] These values of k_A are uncertain. [b] These values of R_c are not the instantaneous values, $(k_A + k_B)/k_A$, but are equal to $\Delta(O_3)/\Delta(H_2O_2)$ for a time interval in which there was a 30% decrease in the concentration of ozone. The corresponding value in the blank experiment is 7.8.
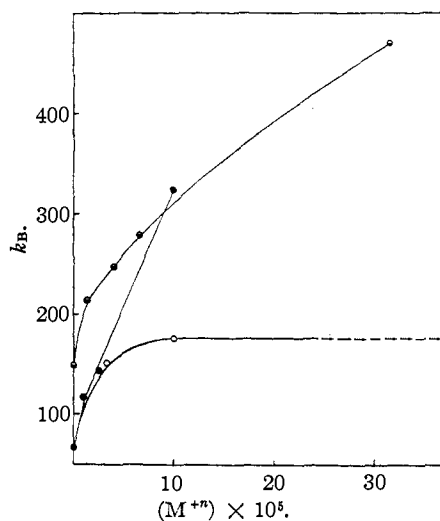

Fig. 5.—Variation of k_B with the concentration of various metal ion catalysts, cf. Tables IX and X: ◖, cobaltous ion; ●, praseodymium ion; ○, copper ion.

It may be concluded that there are at least two catalytic processes. Characteristic of one of these is the gradual, linear rise of k_B with increasing concentration of the catalyst. This effect, which is shown at moderate concentrations of Co^{++} and Pr^{+3}, but not of Cu^{++}, can be attributed to reactions (1a) and (1b).

To account for the sharp initial rise of k_B, ob-

served at low concentrations of the three metal ions, another process is necessary. The results with copper ion in the presence of chloride are believed to be typical for this process. A reasonable hypothesis is that Cu^{++} acts as a catalyst by decreasing the efficiency of the chain breaking steps—which in this instance involve chloride ion and atomic chlorine. It seems probable that the oxidation of Cu^{++} by atomic chlorine and the reduction of the product by hydrogen peroxide are rapid processes. It follows that a moderate concentration of copper ion may lower the steady state concentration of atomic chlorine to such an extent that inhibition by chloride ion becomes negligible. Further additions will then have no effect and, as has been observed, k_B will reach a limiting value. A process of this kind may operate with other catalysts in the presence of chloride ion or other inhibitors.

Certain observations are not explained by these two processes, and will require a more detailed study of particular cases. Among these are the decrease in the consumption ratio, R_c, with increasing concentration of Co^{++} or Cu^{++}, and the relatively great catalysis of reaction A observed with even low concentrations of Ag^+.

Expt. III(2) showed that formic acid catalyzed reactions A and B, although by analogy with the aliphatic acids it was expected to be an inhibitor. Some experiments on the reaction between formic acid and ozone are presented in Table XI. In analyzing the mixtures of ozone and formic acid the ozone was determined as usual; the formic acid remained in the water layer and was determined by a permanganate method. k_1' and k_2' are defined by the expressions

$$-d(HCOOH)/dt = k_1'(O_3)(HCOOH)$$
$$-d(O_3)/dt = k_2'(O_3)(HCOOH)$$

TABLE XI

The Reaction between Formic Acid and Ozone in 0.1 M HClO$_4$

No.	(Cl$^-$)	Time, min.	(HCO-OH) $\times 10^4$	(O$_3$) $\times 10^4$	k_1'	k_2'	k_2'/k_1'
1	None added	0	3.40	14.12	...	...	..
		15	3.16	12.59	6.3	23.6	3.75
		50	2.46	9.91	6.6	25.6	3.88
2	1.2×10^{-3} M	0	2.26	13.03	...	...	
		25	2.07	12.85	...	2.60	
		150	1.70	12.53	...	2.82	ca. 1

The ratio k_2'/k_1' gives the consumption ratio of ozone to formic acid at a particular instant. In Expt. (2) the points in a plot of log (HCOOH) against time did not define a good curve; the con-

sumption ratio, $\Delta(O_3)/\Delta(HCOOH)$, for the whole experiment was very nearly unity.

The values of k_2'/k_1' in Expt. (1) show that the ozone consumed is much in excess of that required to oxidize the formic acid. This catalytic decomposition of ozone is inhibited by chloride ion, Expt. (2). These results suggest that HO is formed in a reaction analogous to (1a) and (1).

$$HC\underset{OH}{\overset{O}{\diagup}} + O_3 \longrightarrow HO + HC\underset{O}{\overset{O}{\diagup}} + O_2$$
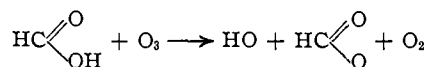
The HO will start the chain decomposition of ozone by reactions (2) and (3), and this will be almost completely eliminated in 10^{-3} M Cl$^-$. Nothing can be said at present about the fate of the formate radical.

The general behavior of inhibitors and catalysts in the present investigation may be summed up as follows: An inhibitor functions by reacting with the intermediate HO, to form a radical which has a higher probability of giving a stable product; a catalyst functions by increasing the rate of formation of HO and HO$_2$ (by reacting with ozone and hydrogen peroxide), and/or by decreasing the efficiency of the chain-breaking step. Whenever an inhibitor in its reaction with HO forms a radical which provides a new chain path for reaction A or B, it will tend to catalyze this reaction. Thus the substitution of nitrate ion for perchlorate resulted in catalysis of reaction A, although reaction B was inhibited. Similarly the chloride ion inhibitor provides a new path for A, and acetic acid one for B; but in these cases the new chain paths are shorter than the original HO, HO$_2$ chains.

III. Rate Laws in the Presence of the Inhibitor, Chloride Ion

Measurements of the rates of reactions A and B inhibited by chloride ion have been used to test rate laws based on intermediate reactions of the radicals hydroxyl, perhydroxyl and atomic chlorine. If we assume that chain termination is completed by the reactions

$$Cl + Cl \overset{k_7}{\longrightarrow} Cl_2 \qquad (7)$$
$$Cl_2 + H_2O_2 = 2H^+ + 2Cl^- + O_2 \qquad (8)$$
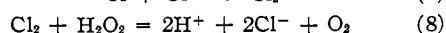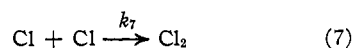
and that all the steps (1) to (8) are practically unidirectional,[29] we obtain for the rates of A and B the expressions

(29) Except for reaction (5), $-\Delta F°$ for each of the reactions succeeding (1) is large. For (5) to be mainly unidirectional, as is required by the kinetic data, we must assume it to be favored on hydration of Cl and HO gases.

$$-d(H_2O_2)/dt = 2k_1P + k_6(Cl)(H_2O_2) + k_4(HO)(H_2O_2)$$
$$-d(O_3)/dt - (-d(H_2O_2)/dt) = 2k_3(HO)(O_3)$$

The three terms in the expression for the rate of A correspond, respectively, to three paths: a non-chain path by way of reactions (1), (2), (5), (5) repeated, (7), and (8); a chain path by way of reactions (2), (5), and (6), and another chain path by way of reactions (2) and (4). The mechanism gives a single path for B, the chain path by way of reactions (2) and (3).

The expressions for the steady state concentrations of HO and Cl, obtained by the usual methods, are

$$(Cl) = (2k_1P/k_7)^{1/2}$$

$$(HO) = \frac{k_6(2k_1P/k_7)^{1/2}(H_2O_2) + 2k_1P}{k_5(H^+)(Cl^-)}$$

Making use of these relations, and the definition $R_s = (H_2O_2)/(O_3)$, we obtain

$$k_A = 2k_1 + k_6(2k_1R_s/k_7)^{1/2} +$$
$$\quad\text{(i)}\qquad\text{(ii)}\quad \frac{k_4(H_2O_2)[2k_1 + k_6(2k_1R_s/k_7)^{1/2}]}{k_5(H^+)(Cl^-)}\quad\text{I}$$
$$\qquad\qquad\qquad\text{(iii)}$$

$$k_B = \frac{2k_3[k_6(2k_1P/k_7)^{1/2} + 2k_1(O_3)]}{k_5(H^+)(Cl^-)}$$

In the expression for k_A, term (i) corresponds to the non-chain path beginning with reaction (1); and terms (ii) and (iii) to the paths involving reaction of hydrogen peroxide with atomic chlorine and HO, respectively.

Equation I predicts that at high chloride term (iii) will be negligible and that k_A will depend only on the concentration ratio, R_s. When k_A is plotted against $R_s^{1/2}$, a straight line should be obtained and there should be an intercept on the k_A axis equal to $2k_1$.

In Fig. 6 k_A[30] is plotted against $R_s^{1/2}$ for experiments at four concentrations of chloride ion. The concentrations of hydrogen ion and chloride ion and the initial concentrations of hydrogen peroxide are listed below the diagram. The points in the upper part of the diagram correspond to the experiments at 10^{-4} M Cl^-. In this type of plot the results of a single run are represented by a series of points which usually start at the left.

At 10^{-3}, 3×10^{-3} and 5×10^{-3} M Cl^-, the values of k_A fall along straight lines over a wide range of concentrations and concentration ratios. The three lines are consistent with an extrapolation to an intercept, $2k_1$, of 0.28 ± 0.02. Thus, k_1 is equal to 0.14 ± 0.01, which is in good agree-

(30) The (small) correction for the direct reaction between ozone and chloride ion has been applied to the values of k_A at 5 × 10⁻³ and 3 × 10⁻³ M Cl⁻, and for low peroxide also at 10⁻³ M Cl⁻.

ment with the value of 0.13 obtained in the acetic acid study.

The agreement of these values is in itself strong evidence for the chain-breaking steps which have been assumed. The assumption of a reaction such as $HO_2 + Cl = H^+ + Cl^- + O_2$ for destroying the radicals would have given the result that $k_1 = 0.28$.

It was shown by experiment that, when chlorine is added to a mixture of peroxide and ozone in acid solution at 10^{-3} M Cl^-, a rapid quantitative reaction between chlorine and peroxide takes place. An experiment also was done in sulfuric acid solution to determine whether ClO_3^- or ClO_4^- is formed in the reaction. Tests[31] on concentrated portions of such solutions from which the ozone was removed by blowing air through, and the peroxide by decomposition with platinum black, failed to show the presence of either of these substances. Hence, the regeneration of the chloride inhibitor (as in reaction 8) is established by an independent experimental result. This system is therefore an example of true negative catalysis.
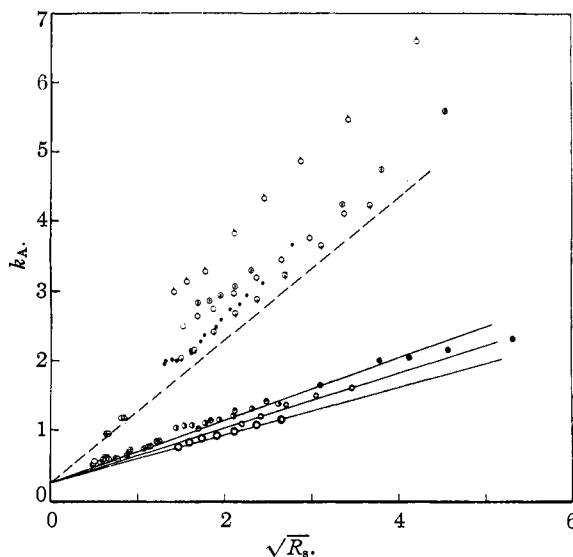

Fig. 6.—The test of Equation I at high chloride:

$(Cl^-) \times 10^4$	$(H_2O_2)_0 \times 10^4$	(H^+)	$(Cl^-) \times 10^4$	$(H_2O_2)_0 \times 10^4$	(H^+)
⊖ 1.0	6.7	0.19	○ 10	3.5	0.19
⊕ 1.0	6.7	.19	⊕ 10	7.2	.19
? 1.0	23.4	.385	⊖ 10	7.2	.19
● 1.0	10.3	.19	⊕ 10	12.9	.19
● 1.0	10.4	.19	⊗ 10	15.1	.19
○ 1.0	22.3	.19	● 10	17.1	.19
◉ 1.0	23.0	.22[a]	◑ 10	26.7	.19
◓ 1.0	20.8	.095	● 10	32.2	.19
			○ 30	25.4	.19
			○ 50	29.4	.19

[a] 0.20 M H_2SO_4.

(31) Spinks and Porter, THIS JOURNAL, **56**, 267 (1934).

The spreading of the points for 10^{-4} M Cl^- in Fig. 6 may be regarded as resulting from term (iii) in Equation I; term (iii) is expected to increase with decreasing chloride and hydrogen ion concentrations. The results at 3×10^{-5} M Cl^-, when plotted in a similar figure, showed a still greater spread.
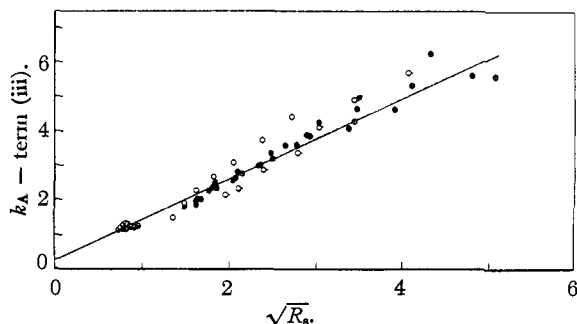

Fig. 7.—The test of Equation II at 3×10^{-5} M Cl^- and 0.19 M $HClO_4$. The initial concentrations of hydrogen peroxide $(H_2O_2)_0 \times 10^4$, are: ◑, 5.5; ◐, 7.3; ○, 5.9; ○-, 11.4; ●, 20.9; ●, 23.0; ●, 20.6; ⊕, 35.6.

The results for k_A in Fig. 6 differ from those predicted in one important respect. It is observed that the slopes of the straight lines obtained in the plot of k_A against $R_s^{1/2}$ at chloride concentrations high enough to make term (iii) negligible, decrease with increasing chloride concentration, while the equation predicts that a single line will be obtained. The theoretical interpretation of this variation is deferred until all the results on k_A have been presented. For the present, Equation I is modified by introducing a term, F_{Cl^-}, to express the dependence of the slopes of the limiting lines on the chloride ion concentration; the modified form is

$$k_A = \underbrace{2k_1 + F_{Cl^-} R_s^{1/2}}_{\text{(i)}} + \underbrace{\frac{k_4(H_2O_2)}{k_5(H^+)(Cl^-)} [2k_1 + F_{Cl^-} R_s^{1/2}]}_{\text{(iii)}} \quad \text{II}$$

If we introduce the experimental values of F_{Cl^-}, obtained for each particular concentration of chloride ion from the plot in Fig. 6, this equation will express the results at 10^{-3} M Cl^- or higher. A test of the equation at lower chloride concentrations where term (iii) becomes appreciable is to plot $[k_A - \text{term (iii)}]$ against $R_s^{1/2}$: a straight line should be obtained at each concentration of chloride ion.

Before term (iii) can be evaluated for known concentrations of peroxide, ozone, chloride ion, and hydrogen ion, k_4/k_5 and F_{Cl^-} for the particular concentration of chloride ion must both be deter-

mined. To do this, k_A, at constant and known values of R_s,(H$^+$) and (Cl$^-$), was plotted against (H_2O_2) for various values of R_s; reasonably good straight lines were obtained. Since the intercept at zero peroxide is equal to $2k_1 + F_{Cl^-} R_s^{1/2}$ the numerical value of F_{Cl^-} was calculated at each concentration of chloride ion. From the slope of each line, $[k_4/k_5(H^+) (Cl^-)] [2k_1 + F_{Cl^-} R_s^{1/2}]$, the corresponding ratio, k_4/k_5, was then determined. The plots of $[k_A - \text{term (iii)}]$ at 3×10^{-5}, 10^{-4}, and 3×10^{-4} M Cl^- are shown in Figs. 7, 8 and 9.

At the lowest chloride concentration, Fig. 7, the agreement is fairly good, though at high R_s and low peroxide (open circles) the deviations exceed the experimental error. These deviations, which are still greater at 10^{-5} M Cl^-, are due at least in part to the presence of other inhibitors (cf. Section I).

In Fig. 8, the data at 10^{-4} M Cl^- are presented. The experiments cover about a 25-fold range in R_s and a 4-fold range in the concentration of hydrogen ion; the theoretical equations correlate these data satisfactorily. The experiment in sulfuric acid solution shows that the specific effect of the acid ion noted in Table V has disappeared at 10^{-4} M Cl^-.
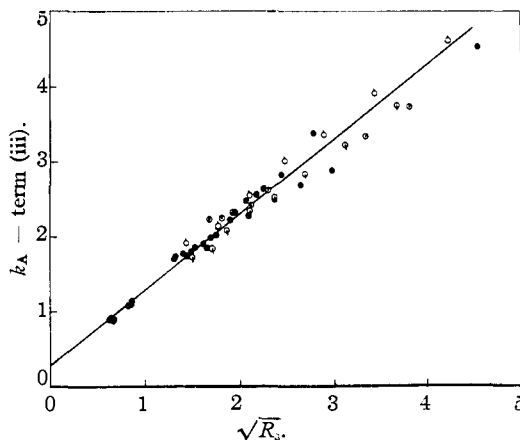

Fig. 8.—The test of Equation II at 10^{-4} M Cl^-:

(Acid)	$(H_2O_2)_0 \times 10^4$
● 0.19 M $HClO_4$	6.7, 6.7, 10.3, 10.4, 22.3
◑ .385 M $HClO_4$	23.4
◔ .095 M $HClO_4$	20.8
◉ .20 M H_2SO_4	23.0

The data at 3×10^{-5} and 10^{-4} M Cl^- include runs in which distilled water from a different source was redistilled and used; runs were also made with redistilled perchloric acid, with hydrogen peroxide prepared from sodium peroxide and perchloric acid, and, as mentioned, with sul-

furic acid instead of perchloric acid. The observed agreement of the data shows that there were no appreciable effects due to accidental traces of foreign substances.

Term (iii) for high values of hydrogen peroxide and low hydrogen ion or chloride ion concentrations amounted to from $^1/_3$ to $^2/_3$ of k_A. The fact that the points cluster about a straight line argues strongly for the validity of the rate expressions for k_A.

At 3×10^{-4} M Cl$^-$, Fig. 9, k_A appears to show an anomalous behavior in a certain range of R_s and ozone concentration. However, the points at low R_s and at high R_s [low (O$_3$)] fall along a line.
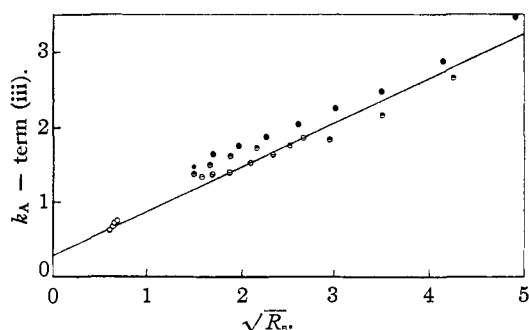

Fig. 9.—The test of Equation II at 3×10^{-4} M Cl$^-$ and 0.19 M HClO$_4$:

(H$_2$O$_2$)$_0$ $\times$ 10^4:   O, 7.1;   ⊖, 23.7;   ◉, 25.6;   ● 30.3.

The data on the variation of k_A with the concentrations of hydrogen peroxide, ozone, chloride, ion, and hydrogen ion are summarized in the equations below.

At 3×10^{-5} M Cl$^-$

$$k_A = 0.28 + 1.16\ R_s^{1/2} +$$
$$\frac{0.0031}{(\text{H}^+)(\text{Cl}^-)}\ (\text{H}_2\text{O}_2)\ R_s^{1/2}\left[1 + \frac{0.28}{1.16\ R_s^{1/2}}\right]$$

At 10^{-4} M Cl$^-$

$$k_A = 0.28 + 1.01\ R_s^{1/2} +$$
$$\frac{0.0028}{(\text{H}^+)(\text{Cl}^-)}\ (\text{H}_2\text{O}_2)\ R_s^{1/2}\left[1 + \frac{0.28}{1.01\ R_s^{1/2}}\right]$$

At 3×10^{-4} M Cl$^-$

$$k_A = 0.28 + 0.54\ R_s^{1/2} +$$
$$\frac{0.0016}{(\text{H}^+)(\text{Cl}^-)}\ (\text{H}_2\text{O}_2)\ R_s^{1/2}\left[1 + \frac{0.28}{0.54\ R_s^{1/2}}\right]$$

At 10^{-3} M Cl$^-$, $k_A = 0.28 + 0.44\ R_s^{1/2}$

At 3×10^{-3} M Cl$^-$, $k_A = 0.28 + 0.38\ R_s^{1/2}$

At 5×10^{-3} M Cl$^-$, $k_A = 0.28 + 0.34\ R_s^{1/2}$

These expressions are equivalent to Equation II for k_A but are not in the same form. In the first expression, $F_{\text{Cl}^-} = 1.16$, $k_4/k_5 = 0.0031/1.16$ and $2k_1 = 0.28$. The alternate form was found convenient in making the calculations since the term in the brackets appears also in the ex-

pression for k_B. Concordant values of k_4/k_5 were obtained: 2.7, 2.8, and 2.9 $\times 10^{-3}$ at 3, 10, and 30 $\times 10^{-5}$ M Cl$^-$, respectively.
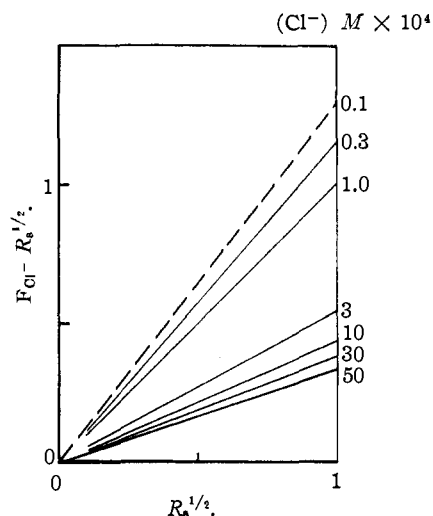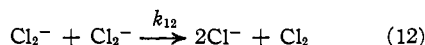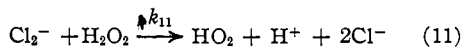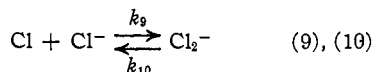

Fig. 10.—Variation of F_{Cl^-}, Equation II, with chloride concentration.

In Fig. 10 the numerical values of F_{Cl^-} shown in the above equations are equal to the slopes of the lines in the diagram. The values of the chloride concentrations are listed on the right-hand side of the diagram. The line for 10^{-5} M Cl$^-$ has been drawn in roughly to agree with values of k_A at very low hydrogen peroxide concentrations, Fig. 14. It will be observed that these lines appear to converge to a limiting slope both at low and at high chloride ion concentrations. Since term (ii) results from reaction of chlorine atoms with peroxide, one is led to the conclusion that chloride ion is reacting with chlorine atoms in some way so as either to decrease the rate of reaction with peroxide and/or to increase the rate at which they react with each other to break chains.

A possible explanation of this effect is suggested by the work of Callow, Griffiths, and McKeown[22] on the photoreaction between hydrogen peroxide and bromine in which inhibition by bromide ion is observed. They found it necessary to assume an equilibrium of the type: Br + Br$^-$ = Br$_2^-$, and chain breaking processes involving Br$_2^-$. Other work (to which Callow, et al., give references) on reactions of bromine and iodine atoms has also suggested such equilibria. By analogy, we can assume an equilibrium of Cl and Cl$^-$ with Cl$_2^-$, and chain breaking steps involving Cl$_2^-$. The mechanism given above will then be complicated by the following additional reactions

$$Cl + Cl^- \underset{k_{10}}{\overset{k_9}{\rightleftharpoons}} Cl_2^- \qquad (9), (10)$$

$$Cl_2^- + H_2O_2 \overset{k_{11}}{\longrightarrow} HO_2 + H^+ + 2Cl^- \qquad (11)$$

$$Cl_2^- + Cl_2^- \overset{k_{12}}{\longrightarrow} 2Cl^- + Cl_2 \qquad (12)$$

A complete treatment would also include the step $Cl_2^- + Cl \longrightarrow Cl_2 + Cl^-$; however, for the sake of simplicity, only the processes obtaining at low and at high chloride concentrations are considered. The intermediate region can probably be averaged fairly well in this way. The present treatment is intended only to show that this added assumption will explain the results.

A rapid equilibrium between Cl, Cl$^-$ and Cl$_2^-$ is assumed, $i.\ e.$, $(Cl)(Cl^-)/(Cl_2^-) = k_{10}/k_9 = K$. Setting up the equations for the steady state concentration as before, one obtains the following results for the stationary concentrations of the intermediates.

$$(Cl_2^-) = \left[\frac{2k_1}{k_{12} + k_7[K/(Cl^-)]^2} P \right]^{1/2} = DP^{1/2}$$

$$(Cl) = \left[\frac{2k_1}{[(Cl^-)/K]^2 k_{12} + k_7} P \right]^{1/2} = EP^{1/2}$$

$$(HO) = \frac{(k_6 E + k_{11} D)P^{1/2}(H_2O_2) + 2k_1 P}{k_5(H^+)(Cl^-)}$$

The only variable in the expression $(k_6 E + k_{11} D)$ is (Cl^-); again representing this chloride dependent expression by the symbol F_{Cl^-}, we obtain for k_A the identical equation II, or the alternative form

$$k_A = 2k_1 + F_{Cl^-} \cdot R_s^{1/2} +$$
$$\frac{k_4 F_{Cl^-} \cdot R_s^{1/2} (H_2O_2)}{k_5(H^+)(Cl^-)} \left[1 + \frac{2k_1}{F_{Cl^-} \cdot R_s^{1/2}} \right] \quad IIa$$

The following considerations will show that the relation $F_{Cl^-} = k_6 E + k_{11} D$ represents the observed variation of F_{Cl^-} with (Cl^-) shown in Fig. 10. As the concentration of chloride is in-
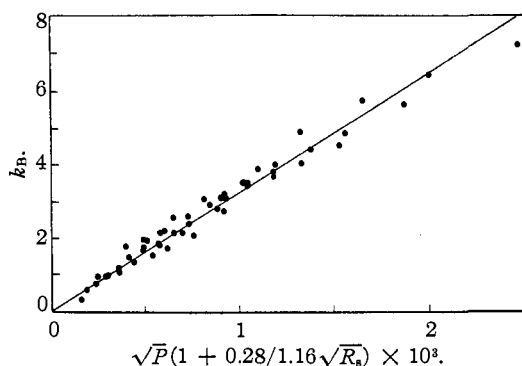

Fig. 11.—The test of Equation III at 3×10^{-5} M Cl$^-$ and 0.19 M HClO$_4$. The experiments are those listed below Fig. 7.

creased, D approaches $(2k_1/k_{12})^{1/2}$, $E \longrightarrow$ zero, and $F_{Cl^-} \longrightarrow k_{11}(2k_1/k_{12})^{1/2}$. This corresponds to the experimental limit approached by F_{Cl^-} at high chloride, Fig. 10, and means that Cl is completely replaced by Cl$_2^-$. At low chloride E approaches zero, $D \longrightarrow (2k_1/k_7)^{1/2}$ and $F_{Cl^-} \longrightarrow k_6(2k_1/k_7)^{1/2}$. This corresponds to the limiting value approached at low chloride, and signifies that Cl$_2^-$ does not play any noticeable role in the reaction. As the limiting value of F_{Cl^-} at low chloride exceeds that at high chloride, $k_6/k_7^{1/2}$ must be greater than $k_{11}/k_{12}^{1/2}$.

The theoretical equation thus has the proper form to express the variation of k_A with all the concentration variables considered, and we may conclude that the mechanism proposed represents satisfactorily the observations on the rate of A in the range of concentrations studied.

The theoretical expression for k_B takes the forms

$$k_B = \frac{2k_3}{k_5(H^+)(Cl^-)} [F_{Cl^-} \cdot P^{1/2} + 2k_1(O_3)]$$

$$\text{or } \frac{2k_3 F_{Cl^-} \cdot P^{1/2}}{k_5(H^+)(Cl^-)} \left[1 + \frac{2k_1}{F_{Cl^-} \cdot R_s^{1/2}} \right] \quad III$$

This equation predicts that if k_B is plotted against $P^{1/2}(1 + 2 k_1/F_{Cl^-} \cdot R_s^{1/2})$, a straight line should be obtained which goes through the origin. F_{Cl^-} is the coefficient of $R_s^{1/2}$ in the equation for k_A, so that $P^{1/2}(1 + 0.28/F_{Cl^-} \cdot R_s^{1/2})$ readily is evaluated.

In Figs. 11, 12 and 13 the data at 3×10^{-5}, 10^{-4}, and 3×10^{-4} M Cl$^-$ are presented. At higher chloride, k_B is too small to permit a test of the equation. Examination of these diagrams shows that a relation of the form predicted is satisfied, for the 25-fold range of (O$_3$) and the 10-fold range of (H$_2$O$_2$) tested, within the limits of experimental error. At 3×10^{-4} M Cl$^-$, k_B is quite small in comparison with k_A and k_c. Since the error in each of these is of the order of 5%, the percentage error in k_B becomes quite large. However, the line through the k_B points at high values of the function plotted as abscissa is correct within 5 to 10%, since it is an average of three experiments which agree closely.

In Fig. 12, the data on the variation of k_B with hydrogen ion concentration are also presented. The broken lines are those predicted by the equation, and the agreement with the experimental points is satisfactory. The points for sulfuric acid are also plotted; when $k_{HSO_4^-}$ is assumed to be 0.024, the dotted line is the one predicted for sulfuric acid of the concentration used.
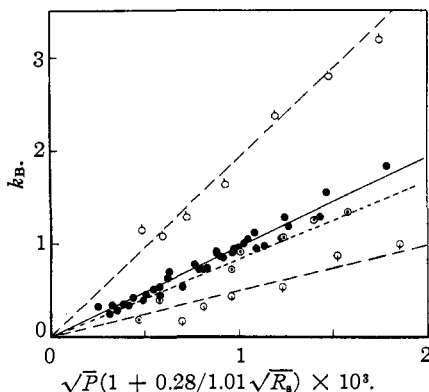
Fig. 12.—The test of Equation III at 10^{-4} M Cl$^-$; cf. Fig. 8 for legend.

We again observe that the specific effect of sulfate ion has disappeared at 10^{-4} M Cl$^-$.
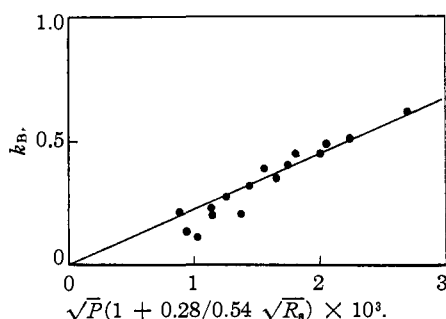

Fig. 13.—The test of Equation III at 3×10^{-4} M Cl$^-$ and 0.19 M HClO$_4$. The experiments are the three, at higher peroxide concentrations, listed below Fig. 9.

The data on k_B are summarized by the equations

At 3×10^{-5} M Cl$^-$

$$k_B = \frac{0.0188}{(H^+)(Cl^-)} \; P^{1/2} \left[1 + \frac{0.28}{1.16 \; R_s^{1/2}} \right]$$

At 10^{-4} M Cl$^-$

$$k_B = \frac{0.0186}{(H^+)(Cl^-)} \; P^{1/2} \left[1 + \frac{0.28}{1.01 \; R_s^{1/2}} \right]$$

At 3×10^{-4} M Cl$^-$

$$k_B = \frac{0.0127}{(H^+)(Cl^-)} \; P^{1/2} \left[1 + \frac{0.28}{0.54 \; R_s^{1/2}} \right]$$

The experimental values of the ratios of the slopes of the lines in the k_B plots at 3×10^{-5}, 10^{-4}, 3×10^{-4}, 10^{-3} M Cl$^-$ are compared below with those predicted by the law of variation with $F_{Cl^-}/(Cl^-)$ required by the theoretical Equation, III

Experimental, 3.36:1.00:0.22:......
$F_{Cl^-}/(Cl^-)$ law, 3.80:1.00:0.19:0.044

The agreement of the experimental and predicted values is improved if allowance is made for two factors which have been neglected in the derivation of Equation III. One of these corrections will raise the values of k_B at 3×10^{-5} M Cl$^-$ relative to the others by several per cent.; on lowering the chloride concentration the influence of other inhibitors becomes appreciable and k_B does not increase as rapidly as is predicted by the assumed mechanism. The other correction will decrease k_B at 10^{-4} and 3×10^{-4} M Cl$^-$ relative to the others by about 8 and 25%, respectively, at 2×10^{-3} M H$_2$O$_2$ and 0.6×10^{-3} M O$_3$; at the higher concentrations of chloride ion k_B approaches finite limits, instead of zero. In Section I this experimental result was attributed to a reaction between ozone and atomic chlorine; the effect of this reaction is relatively small except at low values of k_B and R_s.

As has already been suggested, the experimental results at low chloride deviate widely from those predicted by the mechanism. In Fig. 14, a plot of k_A against $R_s^{1/2}$ for 10^{-5} M Cl$^-$ is presented.
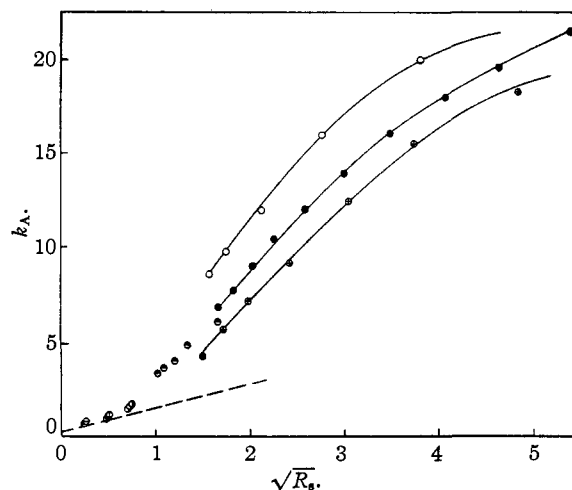

Fig. 14.—Values of k_A at 10^{-5} M added chloride in 0.19 M HClO$_4$: ⊖, (H$_2$O$_2$)$_0$ × 10^4 = 1.0; ◑, 3.6; ◐, 16.7; ⊖, 12.9; ⊕, 11.3; ●, 22.3; ○, 27.7.

An interesting feature of these results, not predicted by the mechanism, is that k_A appears to level off to a constant value at high R_s. The data at low peroxide, however, are still consistent with a limiting line corresponding to term (ii) in the expression for k_A. This line has been dotted in and has the same slope as the corresponding line in Fig. 10.

In Fig. 15, a plot of k_B against $P^{1/2} \left[1 + \frac{0.28}{1.30 \; R_s^{1/2}} \right]$ is presented; the agreement with the rate law has not entirely disappeared. Certain of the points at 3×10^{-5} M Cl$^-$ began to show a little of the de-

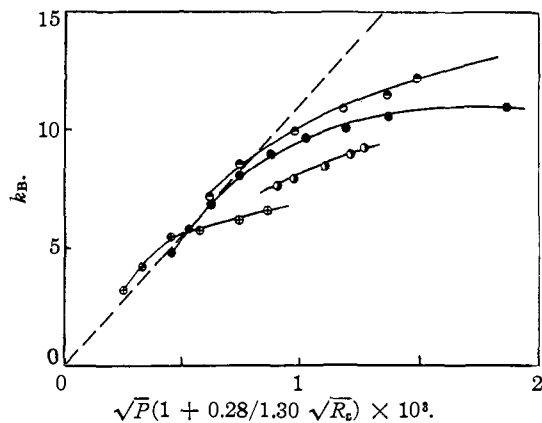viation exhibited by those at high values of $P^{1/2}$ in the present plot.

Fig. 15.—Test of Equation III at 10^{-5} M Cl$^-$, cf. Fig. 14 for legend.

Part of this deviation has been attributed to the effect of other inhibitors. Another possibility, not considered heretofore, but which appears reasonable, is that the chain terminating process $HO_2 + Cl \longrightarrow H^+ + Cl^- + O_2$ may become important. An approximate relation between the stationary concentrations of HO_2 and Cl which should be valid at 3×10^{-5} M Cl$^-$ is

$$(HO_2) = \left[\frac{k_6 R_s (Cl)}{k_2 k_3 (H^+)(Cl^-)} \right]$$

$$[k_3(O_3) + k_4(H_2O_2) + k_5(H^+)(Cl^-)]$$

At lower chloride and high R_s, (HO_2) increases relative to (Cl), and the process $HO_2 + Cl \longrightarrow$ would tend to become more probable than $Cl + Cl \longrightarrow$. An experimental test of a mechanism in which the two processes are competing to break the chains is almost impossible, since the corresponding rate laws are quite involved.

In the range of concentrations in which the rate laws II for A and III for B apply, numerical values of the coefficients have been determined and listed; these enable the specific rates of some of the rate determining steps to be compared with each other.

Examination of the equations derived from the mechanism shows that, if the coefficient of (H_2O_2) $R_s^{1/2}$ in II is compared with the coefficient of $P^{1/2}$ in III, the relative values of k_3 and k_4 may be obtained. The comparison gives the following results: from the numerical data at 3×10^{-5} M Cl$^-$, $k_3 = 3.02$ k_4; from the data at 10^{-4} M Cl$^-$, $k_3 = 3.32$ k_4. Thus we see that HO reacts about three times as rapidly with ozone as it does with hydrogen peroxide. The two corrections for k_B

discussed above will bring the two results into better agreement, mainly by lowering the second one.

A comparison of k_3 and k_5 can also be made. From the data at 10^{-4} M Cl$^-$, $k_3 = 0.0093$ k_5. Thus, HO reacts about 107 times as readily with chloride ion as with ozone at 1 M H$^+$; at 0.19 M H$^+$ the factor will be ca. 20.

Relative values for k_3 and k_4 were also obtained from the acetic acid data. If one considers the mechanism for the reaction suggested in Section I, which assumes that HO reacts with the inhibitor, acetic acid, expressions for k_A and k_B can be derived

$$k_A = k_1 + \frac{2k_4 k_1}{k_{5h}} \frac{(H_2O_2)}{(AcOH)}$$

$$k_B = 2k_3 \frac{2k_1}{k_{5h}} \frac{(O_3)}{(AcOH)} + f(O_3)(H_2O_2)$$

where k_1, k_3 and k_4 have the same meaning as before, and k_{5h} is the specific rate of the reaction of acetic acid with HO. The last term in the expression for k_B represents the residual decomposition of ozone by the organic free radicals. It will be independent of the acetic acid concentration but the form with respect to the variables (H_2O_2) and (O_3) will depend on the chain-breaking step assumed.

Examination of the equations shows that if k_A and k_B are plotted against $1/(AcOH)$ at constant (H_2O_2) and (O_3), the slopes of these lines will give, by comparison, the relative value of k_3 and k_4. The slopes were obtained from Figs. 2 and 3: 4.8×10^{-4} and 32×10^{-4}. The concentration of peroxide was ca. 0.95×10^{-3} M, and that of ozone 1.00×10^{-3} M. These data give the result that $k_3 = 3.2$ k_4. The close agreement with the value from the work on chloride ion is convincing evidence that the same intermediate reacts with the inhibitor in both cases. The relative rates of reaction of ozone and acetic acid with HO can also be obtained. The slope of the line in the plot of k_B against $1/(AcOH)$ is $[4k_1 k_3/k_{5h}]$ (O_3). Since k_1 and (O_3) are known, k_3/k_{5h} can be calculated.

The relative specific rates of reaction of HO with ozone, peroxide, chloride ion and acetic acid, in 0.19 M perchloric acid at 0°, are summarized below.

O_3	H_2O_2	Cl$^-$	AcOH
k_3	$k_4 = 0.32$ k_3	0.19 $k_5 = 20$ k_3	$k_{5h} = 0.16$ k_3

Summary

The method of studying the rates of the two reactions, A and B, which take place in a mixture of ozone and hydrogen peroxide in acid aqueous solution, and the analytical methods used, are described.

It has been shown that bromide ion, chloride ion, aliphatic acids (except formic acid) and alcohols are inhibitors for reaction B, and that the same substances (except bromide ion) inhibit reaction A. Both reactions are chain reactions.

The effect of varying the concentration of acetic acid and of chloride ion, at nearly constant concentrations of ozone, peroxide and acid, and the effect of replacing perchlorate ion by nitrate and by sulfate in the absence of added inhibitors, have been determined.

Differential equations have been found which represent the rates of the chain reactions A and B in the presence of the inhibitor, chloride ion, in acid solution, 0.1 to 0.4 M H$^+$, at 0°. These rate laws are valid for the chloride concentration range 3×10^{-5} to 5×10^{-3} M, and for about 100-fold variation of the hydrogen peroxide–ozone concentration ratio. At lower concentrations of added chloride the action of other inhibitors interferes, and at higher concentrations the yield of reaction A is increased by direct action of ozone on chloride ion.

The results are interpreted by reactions involving HO and HO$_2$. These are formed in a bimolecular reaction between hydrogen peroxide and ozone; its specific rate at 0° has been found by independent experiments with the inhibitors acetic acid and chloride ion to be 0.13 and 0.14 liters moles^{-1} min.$^{-1}$.

HO reacts with ozone, hydrogen peroxide, and the inhibitors (including nitrate ion, sulfate ion and probably perchlorate ion). Of these substances ozone is the only one that must be assumed to react appreciably with HO$_2$.

When acetic acid is the inhibitor, organic free radicals are formed which react with ozone but not with hydrogen peroxide. Atomic chlorine, formed when chloride ion is the inhibitor, reacts much more readily with hydrogen peroxide than with ozone.

The experimental rate laws with chloride ion as inhibitor agree well with those predicted by the proposed mechanism. The relative rates of reaction of HO with chloride ion, ozone, hydrogen peroxide and acetic acid have been determined; the specific rates decrease in this order in 0.19 M H$^+$. Evidence has been found for the equilibrium Cl + Cl$^-$ = Cl$_2^-$.

Certain metal ions, Ce^{+3}, Pr^{+3}, Co^{++}, Cu^{++}, Ag$^+$ and Tl$^+$, and also formic acid, have been found to catalyze reactions A and B; and the effect of varying the concentrations of Pr^{+3}, Co^{++} and Cu^{++} has been studied. It has been shown that there is a large increase in the rate of decomposition of ozone during the oxidation of cobaltous ion, cerous ion and formic acid by ozone; and also during the oxidation of hydrogen peroxide by ceric ion. The results support the theory that HO and HO$_2$ are present as intermediates in reactions A and B. The catalysts operate in general by increasing the rate of formation of the free radicals and/or by decreasing the efficiency of the chain-breaking steps.