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Disproportionation of Chlorous Acid. I. Stoichiometry[1]

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Received July 21, 1967

The disproportionation of chlorous acid was studied at an ionic strength of 2.0 M under a variety of hydrogen ion conditions from 1.2×10^{-3} to 2.0 M and with up to 0.1 M added chloride ion. In the absence of added chloride ion, in 1.2 and 2.0 M perchloric acid at 25°, the stoichiometry can be approximated as: $4HClO_2 \rightarrow 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O$. At the beginning of the reaction less chlorine dioxide than that predicted by the above equation is formed, and, as the reaction proceeds, the relative amount of chlorine dioxide produced increases. The relative amount of chlorine dioxide produced also varies with the hydrogen ion concentration. Chloride ion catalyzes the disproportionation of chlorous acid and also alters the stoichiometry to approximately $5HClO_2 \rightarrow 4ClO_2 + Cl^- + H^+ + 2H_2O$. As the reaction proceeds in the presence of initial chloride ion, less chlorine dioxide than that predicted by the second equation is formed. Also, as the initial concentration of chloride ion is decreased, the relative amount of chlorine dioxide formed decreases. A mechanism which is consistent with these observations is proposed.

Introduction

As part of a detailed study of the properties of chlorine-containing oxidizing agents, reactions of acidified chlorine(III) solutions with various metal ions such as vanadium(II),[3] iron(II),[3] tris(1,10-phenanthroline)-iron(II),[3] chromium(II),[4] uranium(IV),[5] and vanadium(III)[3] have been studied. Since most of these investigations were carried out in up to 2 M perchloric acid solutions, it was necessary to predict the kinetic behavior of chlorous acid under these conditions. If chlorous acid disproportionates at a rate comparable to the rate of the chlorine(III) reaction with the metal ion, the disproportionation reaction may be important in the rate and mechanism of metal ion oxidation. Most of the previous studies of the disproportionation reaction have been carried out in the low pH range in the absence of added chloride ion. The studies reported here were primarily concerned with the stoichiometry of the disproportionation of chlorous acid in high acid and in the presence of added chloride ion. In the paper[6] following, the kinetics of the disproportionation reaction will be discussed.

The over-all stoichiometry of the disproportionation of chlorous acid has been reported by several investigators.[7-13] In an acidic solution, in the absence of added chloride ion which alters the reaction, the stoichiometry has been found to approximate

$$4HClO_2 = 2ClO_2 + ClO_3^- + Cl^- + 2H^- + H_2O \qquad (1)$$

In the presence of appreciable amounts of chloride ion, only very small amounts of chlorate ion have been found and the stoichiometry approximates

$$5HClO_2 = 4ClO_2 + Cl^- + H^+ + 2H_2O \qquad (2)$$

It must be emphasized that although eq 1 and 2 do not exactly describe the stoichiometry, appropriate linear combinations will. Many deviations from eq 1 and 2 have been found.[7-13] Under conditions where reaction 1 predominates, a contribution from reaction 2 can be expected since chloride ion, which catalyzes reaction 2, is produced in reaction 1. Chlorine has been reported as a reaction product under certain conditions, but, generally, it cannot be found as a product since the reaction between chlorine(III) and chlorine is very rapid in acidic solutions.[14]

Experimental Section

Reagents.—Sodium chlorite was obtained from Matheson Coleman and Bell. Analysis of the sodium chlorite showed greater than 99% sodium chlorite and 0.47% sodium chloride.[5] The additional impurity was presumed to be sodium perchlorate. The small amount of sodium chloride present did not have any noticeable effect on the stoichiometry. Chlorine dioxide was prepared by the method of Bray.[15] The purified gas was dissolved in distilled water and stored in the dark at 0°. The molar extinction coefficient (M^{-1} cm^{-1}) of chlorine dioxide was found to be 1242 ± 2 at 3600 Å and 1250 ± 3 at 3585 Å. The concentrations of sodium chlorite and chlorine dioxide solutions were determined iodometrically. Sodium perchlorate was prepared and standardized by the method reported by Gordon and Andrews.[16] Sodium chloride solutions were prepared by dissolving a weighed amount of dried analytical reagent grade crystals in known amounts of distilled water.

Apparatus.—Figure 1 is a diagram of the reaction vessel[17] which was used in all of the kinetic experiments. It consists essentially of a 50-cc syringe, mounted in a frame such that the volume of the syringe is determined by the position of the turn screw. This reaction vessel is jacketed such that it can be maintained at a constant temperature. The volatility of chlorine dioxide made it necessary to use a vessel from which any air gap could be removed. Otherwise, the chlorine dioxide concentra-

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(1) Part of the thesis of R. G. Kieffer, presented to the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) G. Gordon, R. Miyatake, B. Shakhashiri, P. H. Tewari, and C. McCormick, unpublished results.

(4) R. Thompson and G. Gordon, *Inorg. Chem.*, **5**, 557, 562 (1966).

(5) G. Gordon and F. Feldman, *ibid.*, **3**, 1728 (1964).

(6) R. G. Kieffer and G. Gordon, *Inorg. Chem.*, **7**, 239 (1968).

(7) B. Barnett, Ph.D. Dissertation, University of California, 1935.

(8) M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, **32**, 899 (1940).

(9) J. F. White, M. C. Taylor, and G. P. Vincent, *ibid.*, **34**, 782 (1942).

(10) W. Buser and H. Hanisch, *Helv. Chim. Acta*, **35**, 3547 (1952).

(11) F. Böhmlander, *Wasser-Abwasser*, **104**, 518 (1963).

(12) H. Taube and H. Dodgen, *J. Am. Chem. Soc.*, **71**, 3330 (1949).

(13) H. Baier, *Melliand Textilber.*, **32**, 141 (1951).

(14) R. Emmenegger and G. Gordon, *Inorg. Chem.*, **6**, 633 (1967).

(15) W. C. Bray, *Z. Physik. Chem.*, **54**, 569 (1906).

(16) G. Gordon and A. Andrews, *Inorg. Chem.*, **3**, 1733 (1964).

(17) This reaction vessel was designed and constructed by R. A. Silverman, University of Maryland, 1965.

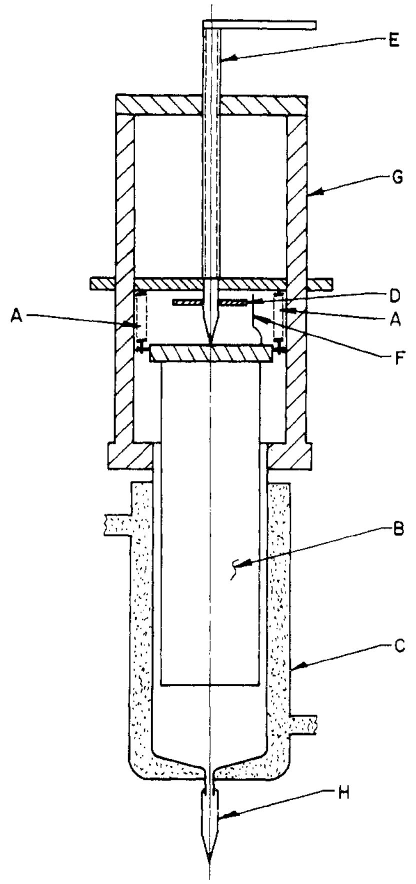

Figure 1.—Reaction vessel (courtesy of R. A. Silverman): A, retaining springs; B, 50-cc Pyrex syringe; C, glass water jacket; D, calibrated wheel; E, screw; F, indicator; G, brass frame; H, glass needle.

tion in the solution would depend on the size of the air gap since the volatile chlorine dioxide would equilibrate with the air. This reaction vessel is, in principle, a "shrinking bottle" which makes it possible to remove accurately an aliquot of solution for analysis by turning the screw without forming an air gap in the vessel. At the beginning of each experiment the reaction vessel was inverted and any air gap was removed. In very fast reactions, which contained large initial chloride ion concentrations, it was not practical to remove completely the air gap initially.

Experimental Procedure.—In each experiment a known amount of sodium chlorite was injected into a perchloric acid solution which contained the proper amount of sodium perchlorate to maintain ionic strength. All of the experiments were carried out at an ionic strength of 2 M unless otherwise indicated. In those experiments where chloride ion was added, the required amount of standardized sodium chloride solution was added to the perchloric acid–sodium perchlorate solution. For each experiment, two solutions were prepared; one was placed in a 1-cm cylindrical quartz cell and placed in a Cary 14R spectrophotometer; the other solution was placed in a 50-cc reaction vessel. The solution in the spectrophotometer was analyzed for chlorine dioxide at 3585 or 3600 Å. Samples from the 50-cc reaction vessel periodically were titrated iodometrically for the total chlorine(III) and chlorine dioxide content. With 0.1–0.2 M hydrogen ion, the chlorate ion formed in the reaction was not determined by means of the iodometric titration. In experiments where the hydrogen ion concentration was greater than 0.2 M, the acidity of the samples was reduced to 0.2 M by adding sodium hydroxide before quenching the reaction with sodium iodide.

The chlorate ion concentration was calculated from the loss in oxidizing power of the solution. It was assumed that chlorate ion was the only higher oxidized species in the disproportionation reaction of chlorous acid. The experiments reported here and those of previous workers afford no evidence for the formation of sodium perchlorate or oxygen. Also, the assumption of only chlorate, chlorine dioxide, and chloride ion as products results in reasonable stoichiometric predictions.

The concentration of chlorine(III) was obtained by subtracting the chlorine dioxide concentration, obtained in the parallel spectrophotometric determination, from the titration value. The chloride ion concentration was obtained from chlorine balance. In this way it was possible to obtain the concentration of the reactant—chlorous acid—and the products—chlorine dioxide, chlorate ion, and chloride ion—as a function of time.

In a typical experiment, 2.7 ml of a perchloric acid–sodium perchlorate solution plus sodium chloride, in the experiments where it was added initially, was placed in the 1.0-cm cell. In addition, 36.97 ml of the same solution was placed in a 50-ml erlenmeyer flask. The cell was brought to the appropriate temperature in the thermostated cell compartment of the spectrophotometer. The solution in the 50-ml erlenmeyer flask and the stock sodium chlorite solution were also maintained at the temperature of the reaction. The sodium chlorite solution was prepared by adding a weighed amount of analytical grade sodium chlorite crystals to a measured amount of deionized distilled water. The exact concentration of the sodium chlorite solution was obtained by iodometric titration. Into the acid-containing 1.0-cm cell, 0.5983 ml of the sodium chlorite solution was injected with a calibrated syringe, and the formation of chlorine dioxide was followed spectrophotometrically. Into the acidic solution contained in the 50-ml erlenmeyer flask, 8.186 ml of the sodium chlorite solution was injected by a calibrated syringe. This solution was rapidly transferred to the 50-cc reaction vessel, and the air gap in the vessel was removed by inverting the vessel. Periodically, samples were removed from the 50-cc reaction vessel and titrated iodometrically with a 1-ml Manostat microburet. The use of the microburet made it possible to carry out accurate and rapid titrations approximately every 2–3 min on relatively small samples. In some experiments, the reactants were mixed and transferred to the 50-cc reaction vessel, and an aliquot of this solution was placed in the 1.0-cm cell. These experiments agreed within experimental error with those performed in the usual manner. Each reported datum point corresponds to the results of replicate runs.

Both the Cary 14R cell compartment and the 50-cc reaction vessel were jacketed such that water from a constant-temperature bath could be circulated about the samples in order to maintain constant temperature ±0.5° for the reaction.

Loss of Chlorine Dioxide.—Since in all of the experiments a volatile gas, chlorine dioxide, was formed, experiments were carried out to determine how much chlorine dioxide was lost due to evaporation both in the cylindrical spectrophotometric cell and in the 50-cc reaction vessel. Under the conditions of our experiments, the average amount of chlorine dioxide lost from the spectrophotometric cell during the first 0.5 hr was 1.6 ± 0.6%; during the first hour, 2.6 ± 0.8%; and during the second and third hours, 0.9 ± 0.5 and 0.5 ± 0.3%, respectively. The irreproducibility of the chlorine dioxide *vs.* time data in replicate experiments could almost entirely be attributed to the irreproducibility found in the chlorine dioxide loss data. Less than 2% of the chlorine dioxide was lost from the 50-cc reaction vessel in 6 hr. This resulted in the excellent reproducibility (a few parts per thousand) of the titration data obtained from replicate experiments. The stock solutions of sodium chlorite showed no evidence of decomposition even after 4 days. The effect of room light on the reaction was shown to be negligible.

Results

Since the stoichiometry was found to change with time and since ultimately we were interested in the rate and mechanism of the reaction,[6] in each experiment the stoichiometry of the reaction was determined as a function of time. The coefficients m, n, q, and p in eq 3

$$m\mathrm{HClO_2} \longrightarrow n\mathrm{ClO_2} + q\mathrm{ClO_3^-} + p\mathrm{Cl^-} \qquad (3)$$

were obtained. The data in Table I show that at 2.0 M hydrogen ion concentration with no initial chloride ion present, the stoichiometry of the reaction, after a time equivalent to 1 half-life,[18] can be approximated by eq 1. At the beginning of the reaction less chlorine dioxide than that predicted by eq 1 is formed, and as the reaction proceeds, the relative amount of chlorine dioxide increases and the relative amount of chlorate ion decreases. This trend of relatively more chlorine dioxide produced with time was found at all of the hydrogen ion concentrations studied above 0.7 M.

TABLE I

STOICHIOMETRY OF THE REACTION IN THE ABSENCE OF INITIAL CHLORIDE ION[a]

Time, min	n/m ($\mathrm{ClO_2}$)	q/m ($\mathrm{ClO_3^-}$)	% $\mathrm{HClO_2}$ decomposed
5.4	0.29	0.43	5.2
12.8	0.37	0.36	7.8
24.5	0.37	0.35	13.0
39.5	0.42	0.32	17.5
56.8	0.43	0.30	23.0
73.6	0.45	0.29	27.5
98.4	0.47	0.28	33.8
121.3	0.48	0.27	39.1
149.3	0.49	0.26	44.7
180.2	0.50	0.25	50.2
206.5	0.50	0.25	54.5
243.7	0.51	0.24	59.9
271.2	0.52	0.23	63.5
298.4	0.53	0.23	66.2
312.0	0.53	0.23	67.5

[a] Conditions: 7.13×10^{-3} M $\mathrm{NaClO_2}$, 2.0 M $\mathrm{HClO_4}$, and 2.0 M ionic strength at 25 ± 0.5°. The stoichiometric coefficients n/m, q/m, and p/m are not independent but are related by the chlorine and electron balance; thus, $(n/m) + (p/m) + (q/m) = 1$ and $4(p/m) + 5(q/m) - (p/m) = 3$. Each reported stoichiometric coefficient corresponds to the instantaneous species concentrations at time t.

Table II shows that the relative amount of chlorine dioxide formed, at the half-life, decreases as the hydrogen ion concentration is decreased from 2.0 to 0.49 M. As the hydrogen ion concentration is lowered further from 0.49 to 2.31×10^{-3} M, the relative amount of chlorine dioxide produced increases.

TABLE II

AVERAGE STOICHIOMETRY AT THE HALF-LIFE FOR DIFFERENT HYDROGEN ION CONCENTRATIONS IN THE ABSENCE OF ADDED CHLORIDE ION[a]

$[\mathrm{H^+}]$, M	n/m ($\mathrm{ClO_2}$)	q/m ($\mathrm{ClO_3^-}$)
2.0	0.49	0.26
1.6	0.47	0.28
1.2	0.47	0.28
0.7	0.43	0.31
0.492	0.41	0.33
0.2	0.42	0.32
0.106	0.43	0.31
3.3×10^{-3}	0.63[b]	0.14
2.3×10^{-3}	0.65[b]	0.13

[a] Conditions: $(3.6\text{–}7.2) \times 10^{-3}$ M $\mathrm{NaClO_2}$ and 2.0 M ionic strength with $\mathrm{NaClO_4}$ at 25 ± 0.5°. [b] Stoichiometric coefficients measured at the quarter-life. Within experimental error, the stoichiometry at the half-life is independent of the initial $\mathrm{NaClO_2}$ concentration in the range studied.

The data in Table III show that in the presence of 0.1 M chloride ion the stoichiometry initially approximates eq 2. As the reaction proceeds, the relative amount of chlorine dioxide decreases and the relative amount of chlorate ion increases.

TABLE III

STOICHIOMETRY OF THE REACTION WITH ADDED CHLORIDE ION[a]

Time, min	n/m ($\mathrm{ClO_2}$)	q/m ($\mathrm{ClO_3^-}$)	% $\mathrm{HClO_2}$ decomposed
2.7	0.79	0.01	23.7
5.9	0.79	0.01	43.5
8.6	0.76	0.03	57.6
11.5	0.77	0.03	67.5
14.5	0.76	0.03	75.2
17.5	0.76	0.03	80.9
20.3	0.76	0.04	84.5
23.1	0.75	0.04	87.6
26.0	0.75	0.04	89.9
28.8	0.74	0.05	91.8

[a] Conditions: 2.00×10^{-4} M $\mathrm{NaClO_2}$, 0.1 M NaCl, 1.2 M $\mathrm{HClO_4}$, and 2.0 M ionic strength with $\mathrm{NaClO_4}$ at 25 ± 0.5°.

The data in Table IV show that as the amount of chloride ion initially added increases, the relative amount of chlorine dioxide produced also increases. The data in Table V show that, with chloride ion present, less chlorine dioxide is formed as the hydrogen ion concentration is lowered from 2.0 to 0.2 M. This suggests that hydrogen ion favors a chlorine dioxide producing path over a chlorate-producing path. The effect of ionic strength is relatively small. An increase in ionic strength from 2.0 to 4.0 M results in an increase in the relative amount of chlorine dioxide produced. For example, with $(3.6\text{–}7.2) \times 10^{-3}$ M sodium chloride in 2.0 M perchloric acid and at 25°, the stoichiometric coefficient for $\mathrm{ClO_2}$ (n/m) changes from 0.49 to 0.55 in 2.0 and 4.0 M ionic strengths, respectively.

TABLE IV

AVERAGE STOICHIOMETRY AT THE HALF-LIFE FOR DIFFERENT INITIAL CHLORIDE ION CONCENTRATIONS[a]

$[\mathrm{Cl^-}]$, M	n/m ($\mathrm{ClO_2}$)	q/m ($\mathrm{ClO_3^-}$)
0.1	0.79	0.01
0.04	0.76	0.03
0.01	0.75	0.04
6.77×10^{-3}	0.73	0.06
2×10^{-3}	0.63[b]	0.14
6.77×10^{-4}	0.55	0.21
6.77×10^{-5}	0.48	0.27
$<10^{-7}$	0.47	0.28

[a] Conditions: $(1.2\text{–}7.2) \times 10^{-3}$ M $\mathrm{NaClO_2}$, 1.2 M $\mathrm{HClO_4}$, and 2.0 M ionic strength with $\mathrm{NaClO_4}$ at 25 ± 0.5°. [b] Conditions: 1.32 M $\mathrm{HClO_4}$ and 2.12 M ionic strength.

TABLE V

AVERAGE STOICHIOMETRY AT THE HALF-LIFE, AT DIFFERENT HYDROGEN ION CONCENTRATIONS, WITH ADDED CHLORIDE ION PRESENT[a]

$[\mathrm{H^+}]$, M	n/m, ($\mathrm{ClO_2}$)	q/m, ($\mathrm{ClO_3^-}$)
2.0	0.77	0.03
1.2	0.76	0.03
0.2	0.70	0.08

[a] Conditions: $(1.37\text{–}7.2) \times 10^{-3}$ M $\mathrm{NaClO_2}$, 0.04 M NaCl, and 2.0 M ionic strength with $\mathrm{NaClO_4}$ at 25 ± 0.5°. The stoichiometric coefficients can also be represented by appropriate linear combinations of eq 1 and 2. In 2.0 M acid this corresponds to an over-all contribution of only 10% by eq 1 and 90% by eq 2. However, at 0.2 M acid, these coefficients correspond to a 33% contribution by eq 1 and only a 66% contribution by eq 2 to the over-all stoichiometry.

The data in Table VI show that at low hydrogen ion concentrations, 0.49 to 1.21×10^{-3} M, the relative amount of chlorine dioxide produced decreases with time.

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[18] The half-life is defined as the time it takes for half the original chlorous acid to decompose.

Table VI

Stoichiometry at Low Hydrogen Ion Concentration in the Absence of Added Chloride Ion[a]

Time, min	n/m (ClO_2)	q/m (ClO_3^-)	% $HClO_2$ decomposed	Time, min	n/m (ClO_2)	q/m (ClO_3^-)	% $HClO_2$ decomposed
2.6	0.65	0.13	12.1	25.6	0.63	0.14	29.1
5.4	0.63	0.14	16.8	29.4	0.62	0.15	31.0
8.5	0.65	0.13	19.5	35.2	0.61	0.16	33.0
11.6	0.63	0.14	22.4	38.7	0.61	0.16	34.1
14.9	0.63	0.14	24.4	44.3	0.60	0.16	35.8
18.8	0.63	0.14	26.6	48.7	0.60	0.16	36.7
22.4	0.63	0.14	28.1	58.2	0.60	0.17	39.0

[a] Conditions: $7.19 \times 10^{-3}\ M$ $NaClO_2$, $3.33 \times 10^{-3}\ M$ H^+, and 2.0 M ionic strength with $NaClO_4$ at 25 ± 0.5°.

Initially added chlorate ion and chlorine dioxide had no noticeable effect on the stoichiometry.

Discussion

All of the stoichiometric observations can be discussed in terms of the following mechanism: path 1: uncatalyzed

$$\mathrm{HClO_2 + HClO_2 \xrightarrow{\mathit{R}_1} HOCl + H^+ + ClO_3^-} \qquad (4)$$

$$\mathrm{HOCl + HClO_2 \xrightarrow{\mathit{R}_2} [Cl{-}Cl{<}^{O}_{O}] + H_2O} \qquad (5)$$

$$\mathrm{HOCl + H^+ + Cl^- \overset{\mathit{K}_1}{\rightleftarrows} Cl_2 + H_2O} \qquad (6)$$

$$\mathrm{Cl_2 + HClO_2 \xrightarrow{\mathit{R}_3} [Cl{-}Cl{<}^{O}_{O}] + H^+ + Cl^-} \qquad (7)$$

$$\mathrm{[Cl{-}Cl{<}^{O}_{O}] + H_2O \overset{\mathit{R}_4}{\rightleftarrows} Cl^- + ClO_3^- + 2H^+} \qquad (8)$$

$$\mathrm{2[Cl{-}Cl{<}^{O}_{O}] \xrightarrow{\mathit{R}_5} Cl_2 + 2ClO_2} \qquad (9)$$

path 2: catalyzed by chloride ion

$$\mathrm{HClO_2 + Cl^- \longrightarrow products} \qquad (10)$$

path 3: uncatalyzed—low hydrogen ion concentrations

$$\mathrm{HClO_2 + ClO_2^- \longrightarrow [HClO_2{-}ClO_2^-]^* \longrightarrow products} \qquad (11)$$

This mechanism is essentially the same as that proposed by Taube and Dodgen.[12] Path 3 has been added in order to explain the stoichiometric and kinetic[6] results obtained at low hydrogen ion concentrations. Equations 5–9 were proposed by Taube and Dodgen in order to explain the results of chlorine tracer experiments on the reactions between chlorine, or hypochlorous acid, and chlorous acid. Reaction 4 is proposed as the rate-determining step in path 1 and R_2 and R_3 are much more rapid than R_1 with $R_3 > R_2$.[15] Reaction 10 is proposed as the rate-determining step for path 2.

The stoichiometry corresponding to path 1 is eq 1 if $R_4 \ll R_5$.

$$\mathrm{2HClO_2 \longrightarrow HOCl + H^+ + ClO_3^-} \qquad (12)$$

$$\mathrm{HOCl + 2HClO_2 \longrightarrow 2ClO_2 + Cl^- + H_2O + H^+} \qquad (13)$$

$$\mathrm{4HClO_2 \longrightarrow 2ClO_2 + ClO_3^- + Cl^- + H_2O + 2H^+} \qquad \text{(over-all)} \quad (1)$$

The stoichiometry appropriate to path 2 is eq 2 if $R_4 \ll R_5$.

$$\mathrm{HClO_2 + Cl^- + H^+ \longrightarrow 2HOCl} \qquad (14$$

$$\mathrm{2(HOCl + 2HClO_2 \longrightarrow 2ClO_2 + Cl^- + H_2O + H^+)} \qquad (15)$$

$$\mathrm{5HClO_2 \longrightarrow 4ClO_2 + 2H_2O + H^+ + Cl^-} \qquad \text{(over-all)} \quad (2)$$

With respect to path 1, it would be expected that at the beginning of the reaction when the concentration of the (Cl_2O_2) intermediate is low, relatively more chlorate would be produced by reaction 8. As the concentration of (Cl_2O_2) increases to its steady-state concentration, the second-order process, eq 9, becomes more important as compared to the first-order process, eq 8. Consequently, the relative amount of chlorine dioxide produced *via* eq 9 should increase with time. Path 1 also produces chloride ion. As the chloride ion concentration increases, the contribution from path 2 to the over-all stoichiometry increases. Since path 2 produces almost exclusively chlorine dioxide and very little chlorate, relatively more chlorine dioxide production is expected as the reaction proceeds. This is borne out by the data shown in Table I.

As shown in Table II, as the hydrogen ion concentration increases from 0.492 to 2.0 M, the amount of chlorine dioxide produced slightly increases. An increase in hydrogen ion concentration favors the more rapid production of (Cl_2O_2) since R_2 would appear to depend on the hydrogen ion concentration. Also, an increase in the hydrogen ion concentration increases the amount of chlorine relative to the amount of hypochlorous acid as shown by eq 6. Chlorine reacts more rapidly with chlorous acid to produce the intermediate than does hypochlorous acid itself.[14] Thus, at higher hydrogen ion concentrations (Cl_2O_2) is formed more rapidly and the relatively higher concentration of the intermediate favors the second-order process, eq 9, which produces chlorine dioxide. At lower hydrogen ion concentrations less intermediate is formed and the first-order process, eq 8, which produces chlorate, is relatively more important. The increase in the amount of chlorine dioxide formed as the hydrogen ion concentration decreases from 0.492 to 2.31×10^{-3} M, as noted in Table II, is readily explained by assuming that path 3, which becomes more important as the hydrogen ion concentration decreases, produces predominantly chlorine dioxide.

The data obtained in experiments where the initial concentration of chloride ion was high, as shown in Table III, are consistent with path 2. The stoichiometry with chloride ion present does not correspond exactly to eq 2 which is presumably due to the ever present contribution from path 1 and also from reaction 8. As the data in Table IV show, for initial chloride ion concentrations of 6.8×10^{-3} to 0.1 M, path 2 predominates over path 1 and very little chlorate ion is formed. As the initial chloride ion concentration decreases, the contribution from path 1 increases and more chlorate ion is formed. As the reaction proceeds, the results in Table III would be consistent with a decrease in the concentration of (Cl_2O_2) and a subsequent increase in the production of chlorate by the first-order process shown in eq 8. The results in Table V are consistent with the previous observation that higher hydrogen ion concentrations favor the more rapid production of (Cl_2O_2) and, consequently, the formation of relatively more chlorine dioxide since both parts, R_4 and R_5, appear to have similar hydrogen ion dependences.

Details of the mechanism of path 3 are not known, but it must produce more chlorine dioxide than is produced by path 1. This is necessary since the data in Table II indicate that at low hydrogen ion concentrations, chlorine dioxide is produced in amounts greater than that corresponding to eq 1. The contribution from path 3 appears to be important only when the hydrogen ion concentration is in the 0.49 to 10^{-4} M range which corresponds to the presence of appreciable amounts of both chlorite ion and chlorous acid. The calculations shown in Table VII indicate that above a hydrogen ion concentration of 0.49 M there is less than 1% chlorite ion present; also if the hydrogen ion concentration is less than 10^{-4} M, there is less than 2% chlorous acid present in the solution. The maximum contribution from path 3 should be at a hydrogen ion concentration of 4.9×10^{-3} M when equivalent amounts of chlorite ion and chlorous acid are present. The data in Table VI show that at the low hydrogen ion concentrations where path 3 predominates, the relative amount of chlorine dioxide produced decreases with time. This is also consistent with a greater contribution from path 1 as the reaction proceeds.

TABLE VII

RELATIVE AMOUNT OF CHLORITE ION PRESENT AS A FUNCTION OF THE HYDROGEN ION CONCENTRATION[a]

$[H^+]$, M	$[ClO_2^-]/[HClO_2]$	% ClO_2^-	$[H^+]$, M	$[ClO_2^-]/[HClO_2]$	% ClO_2^-
2.0	0.245×10^{-2}	0.245	10^{-2}	4.9×10^{-1}	32.9
1.2	0.483×10^{-2}	0.48	4.9×10^{-3}	1.0	50.0
0.7	0.75×10^{-2}	0.75	10^{-3}	4.9	83.1
0.49	1.00×10^{-2}	0.99	10^{-4}	49	98.0
0.2	2.45×10^{-2}	2.45	10^{-5}	490	99.8
0.1	4.9×10^{-2}	4.7			

[a] For the purpose of these calculations a value of 4.9×10^{-3} was used for K_a at 25°: F. Tachiki, *J. Chem. Soc. Japan*, **65**, 346 (1944).

Acknowledgments.—This research was supported by the National Science Foundation under Grant GP-5010. The computer time for this project was supported in part through the facilities of the Computer Science Center of the University of Maryland.

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Disproportionation of Chlorous Acid. II. Kinetics[1]

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Received July 21, 1967

Kinetic data are presented for the disproportionation of chlorous acid at an ionic strength of 2.0 M under a variety of hydrogen ion conditions from 1.2×10^{-3} to 2.0 M and with up to 0.1 M added chloride ion concentration. At 1.2 and 2.0 M hydrogen ion concentrations and at 25°, the rate law is

$$\frac{-d[HClO_2]}{dt} = k_1[HClO_2]^2 + \frac{k_2[HClO_2][Cl^-]^2}{K + [Cl^-]}$$

The parameters k_1 and K are independent of the hydrogen ion concentration and correspond to 1.17×10^{-2} M^{-1} sec^{-1} and 0.0012 M, respectively. In solutions which contain 1.2 M $HClO_4$, k_2 is 1.57×10^{-2} M^{-1} sec^{-1}, and in 2.0 M $HClO_4$, k_2 is 3.00×10^{-2} M^{-1} sec^{-1}. The results are discussed in terms of a detailed mechanism.

Introduction

In the previous paper,[3] the stoichiometry of the disproportionation of chlorous acid was reported. In view of the marked effect of chloride and hydrogen concentrations on the stoichiometry of the reaction and the questions as to the effect of these species on the over-all rate of this reaction, we have undertaken a detailed study of the rate of disproportionation of chlorous acid as a function of these species in an attempt to verify the proposed mechanism.

Alkaline solutions of sodium chlorite are stable for periods of up to 1 year if light is excluded.[4-6] Even with prolonged boiling, no decomposition occurs.[7] As the pH is lowered, a sodium chlorite solution becomes less stable. Neutral solutions of sodium chlorite are still, however, quite stable if they are kept away from light and heat, but the solutions will decompose slowly if they are heated.[6,7] In contrast to alkaline or neutral solutions, the disproportionation of acidic chlorine(III) solutions occurs at a measurable rate; the rate in-

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(3) R. G. Kieffer and G. Gordon, *Inorg. Chem.*, **7**, 235 (1968).

(4) W. C. Bray, *Z. Physik. Chem.*, **54**, 569 (1906).

(5) F. Foerster and P. Dolsh, *Z. Elektrochem.*, **23**, 137 (1917).

(6) M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, *Ind. Eng. Chem.*, **32**, 899 (1940).

(7) G. M. Nabar, V. A. Shenai, and S. Sundaram, *Indian J. Tech.*, **2**, 7 (1964).