

sistent with the previous observation that higher hydrogen ion concentrations favor the more rapid production of ( $\text{Cl}_2\text{O}_2$ ) 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  $4.9 \times 10^{-3}$   $M$  when equivalent amounts of chlorite ion and chlorous acid are present. The data in Table VI show that at the low hydrogen

TABLE VII  
RELATIVE AMOUNT OF CHLORITE ION PRESENT AS A  
FUNCTION OF THE HYDROGEN ION CONCENTRATION<sup>a</sup>

| [H <sup>+</sup> ],<br><i>M</i> | [ClO <sub>2</sub> <sup>-</sup> ]/<br>[HClO <sub>2</sub> ] | % ClO <sub>2</sub> <sup>-</sup> | [H <sup>+</sup> ],<br><i>M</i> | [ClO <sub>2</sub> <sup>-</sup> ]/<br>[HClO <sub>2</sub> ] | %<br>ClO <sub>2</sub> <sup>-</sup> |
|--------------------------------|-----------------------------------------------------------|---------------------------------|--------------------------------|-----------------------------------------------------------|------------------------------------|
| 2.0                            | $0.245 \times 10^{-2}$                                    | 0.245                           | $10^{-2}$                      | $4.9 \times 10^{-1}$                                      | 32.9                               |
| 1.2                            | $0.483 \times 10^{-2}$                                    | 0.48                            | $4.9 \times 10^{-3}$           | 1.0                                                       | 50.0                               |
| 0.7                            | $0.75 \times 10^{-2}$                                     | 0.75                            | $10^{-3}$                      | 4.9                                                       | 83.1                               |
| 0.49                           | $1.00 \times 10^{-2}$                                     | 0.99                            | $10^{-4}$                      | 49                                                        | 98.0                               |
| 0.2                            | $2.45 \times 10^{-2}$                                     | 2.45                            | $10^{-5}$                      | 490                                                       | 99.8                               |
| 0.1                            | $4.9 \times 10^{-2}$                                      | 4.7                             |                                |                                                           |                                    |

<sup>a</sup> For the purpose of these calculations a value of  $4.9 \times 10^{-3}$  was used for  $K_a$  at 25°: F. Tachiki, *J. Chem. Soc. Japan*, **65**, 346 (1944).

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.

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## Disproportionation of Chlorous Acid. II. Kinetics<sup>1</sup>

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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  $1.2 \times 10^{-3}$  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

$$\frac{-d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + \frac{k_2[\text{HClO}_2][\text{Cl}^-]^2}{K + [\text{Cl}^-]}$$

The parameters  $k_1$  and  $K$  are independent of the hydrogen ion concentration and correspond to  $1.17 \times 10^{-2}$   $M^{-1} \text{sec}^{-1}$  and 0.0012  $M$ , respectively. In solutions which contain 1.2  $M$   $\text{HClO}_4$ ,  $k_2$  is  $1.57 \times 10^{-2}$   $M^{-1} \text{sec}^{-1}$ , and in 2.0  $M$   $\text{HClO}_4$ ,  $k_2$  is  $3.00 \times 10^{-2}$   $M^{-1} \text{sec}^{-1}$ . The results are discussed in terms of a detailed mechanism.

### Introduction

In the previous paper,<sup>3</sup> 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.<sup>4-6</sup> Even with prolonged boiling, no decomposition occurs.<sup>7</sup> 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.<sup>6,7</sup> 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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creases with a decrease in pH.<sup>6-10</sup> The disproportionation reaction is very slow at a pH greater than 4; less than 1 mg of chlorine dioxide/l. of solution is formed in 2 hr with an initial sodium chlorite concentration<sup>8</sup> of  $3.2 \times 10^{-3} M$ . Only if the pH is less than 3 will more than 1% of the sodium chlorite decompose within 10 min. Buser and Hanisch<sup>8</sup> also found that the rate of formation of chlorine dioxide goes through a maximum between pH 2 and 3.

The decomposition reaction of chlorine(III) in an acidic medium is approximately second order with respect to chlorous acid.<sup>7,9-13</sup> Barnett<sup>11</sup> reports that at low acidities where the chlorite ion concentration is greater than the chlorous acid concentration, the rate law is

$$-d[\text{HClO}_2]/dt = k[\text{HClO}_2]^2 \quad (1)$$

with  $k$  equal to  $1.4 M^{-1} \text{ min}^{-1}$  at  $25^\circ$  with an activation enthalpy of 11 kcal/mole. The same rate-determining step of chlorous acid reacting with chlorous acid that was assumed by Barnett<sup>11</sup> has also been proposed by Nabar, Shenai, and Sundaram<sup>7</sup> and by Taube and Dodgen.<sup>10</sup>

White, Taylor, and Vincent<sup>12</sup> found that chlorate ion does not enhance the formation of chlorine dioxide from the disproportionation of chlorous acid. Taube and Dodgen<sup>10</sup> also report no difference in the rate of decomposition of chlorous acid for two solutions with widely different chlorate ion concentrations.

Chloride ion accelerates the decomposition reaction of chlorous acid<sup>4,10,11</sup> and also alters the stoichiometry.<sup>8,10</sup> Barnett<sup>11</sup> and Taube and Dodgen<sup>10</sup> proposed that chlorous acid reacts with chloride ion in the rate-determining step for the chloride ion catalyzed decomposition of chlorous acid.

In this paper we report our observations on the kinetics of the disproportionation of chlorous acid.

### Experimental Section

The apparatus used in these experiments and the preparation of reagents are identical with that reported elsewhere.<sup>3</sup> In principle, the concentrations of chlorite ion, chlorine dioxide, chlorate ion, and chloride ion were collected as a function of time and analyzed mathematically in order to obtain an appropriate rate law.

Many different rate laws were studied in an attempt to fit the experimental data to an empirical equation. All of the calculations were done by computer.<sup>14</sup> Below is given a typical calculation for one of the rate laws studied. Consider the rate law

$$\frac{-d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + k_2[\text{HClO}_2][\text{Cl}^-] \quad (2)$$

By rearranging eq 2 and integrating

$$-f d[\text{HClO}_2] = k_1 f[\text{HClO}_2]^2 dt + k_2 f[\text{HClO}_2][\text{Cl}^-] dt \quad (3)$$

$$-f d[\text{HClO}_2] = [\text{HClO}_2]_0 - [\text{HClO}_2]_t \quad (4)$$

The remaining two integrals were integrated by using a numerical integration which assumed the area under the curve to be a series of trapezoids. Let  $(\text{AZINT}) = \int [\text{HClO}_2]^2 dt$  and  $(\text{ABINT}) = \int [\text{HClO}_2][\text{Cl}^-] dt$ . Equation 3 can be rewritten as

$$[\text{HClO}_2]_0 - [\text{HClO}_2]_t = k_1(\text{AZINT}) + k_2(\text{ABINT}) \quad (5)$$

After rearrangement and substitution

$$Y = k_2 X + k_1 \quad (6)$$

where  $Y = ([\text{HClO}_2]_0 - [\text{HClO}_2]_t)/(\text{AZINT})$  and  $X = (\text{ABINT})/(\text{AZINT})$ . Equation 6 was solved for  $k_1$  and  $k_2$  by the method of least squares with unit weights for each datum point. By substituting the least-squares values of  $k_1$  and  $k_2$  and the experimental value of  $X$  into eq 6,  $YC$  was calculated.

$$YC = k_2 X + k_1 \quad (7)$$

The deviations were computed as

$$\text{DEV} = YC - Y \quad (8)$$

The following were also computed

$$\text{av dev} = \frac{\Sigma |\text{DEV}|}{n} \quad (9)$$

$$\text{std dev} = \sigma = [\Sigma (\text{DEV})^2 / (n - 2)]^{1/2} \quad (10)$$

$$\text{std dev of slope (or } k_2) = \left[ \frac{\sigma^2}{\Sigma (X - \bar{X})^2} \right]^{1/2} \quad (11)$$

where  $\bar{X}$  is the average value of  $X$

$$\text{std dev of the intercept (or } k_1) = \left[ \frac{\sigma^2 \Sigma X^2}{n \Sigma (X - \bar{X})^2} \right]^{1/2} \quad (12)$$

$$\% \text{ dev} = \frac{100(\text{av dev})}{\text{av value of } Y} \quad (13)$$

All of the other rate laws studied were calculated in a similar manner. The per cent deviation was used as an indication of the "goodness of fit" of the experimental data to the rate law under consideration.

### Results and Discussion

The rate of decomposition of chlorous acid varies with the concentrations of the hydrogen ion, chlorite ion, and chloride ion and with the ionic strength and temperature. Table I shows that the rate of decomposition does not vary appreciably with hydrogen ion concentration in the 2.0–0.2  $M$  range in the absence of initial chloride ion. A comparison<sup>15</sup> of  $t_{1/2}$ ,  $t_{1/4}$ , and  $t_{1/8}$  shows that the rate is most affected by the hydrogen ion concentration at the beginning of the reaction where the rate is faster at lower hydrogen ion concentrations although the half-life is fairly constant in this range of acidity. These data suggest that there are at least two rate-determining processes involved. The first would appear to be important at the beginning of the reaction in the  $0.49\text{--}2.31 \times 10^{-3} M$  hydrogen ion range. The second process, which predominates in the 0.7–2.0  $M$  hydrogen ion range, appears to be independent of the hydrogen ion concentration. A third process reflects the autocatalytic effect of chloride ion. With 0.04  $M$  sodium chloride present initially and with  $(3.60 \pm 0.02) \times 10^{-3} M$  sodium chlorite, half-lives of 9.5, 17.2, and 98.5 min were observed with 2.0, 1.2, and 0.2  $M$  hydrogen ion concentrations, respectively. Thus, in the

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(14) The computer time for this project was supported in part through the facilities of the Computer Science Center of the University of Maryland.

(15) Whenever  $t_{1/2}$ , or half-life, is referred to, it indicates the time in minutes it takes for half of the original chlorous acid to decompose. Similarly  $t_{1/4}$  or  $t_{1/8}$  refer to the time in minutes that it takes for one-fourth or one-eighth of the original chlorous acid to decompose.

TABLE I

EFFECT OF HYDROGEN ION CONCENTRATION ON THE RATE OF THE REACTION IN THE ABSENCE OF INITIAL CHLORIDE ION<sup>a</sup>

| [H <sup>+</sup> ] <sub>0</sub> , <i>M</i> | <i>t</i> <sub>1/2</sub> <sup>b</sup> , min | <i>t</i> <sub>1/4</sub> , min | <i>t</i> <sub>1/8</sub> , min |
|-------------------------------------------|--------------------------------------------|-------------------------------|-------------------------------|
| 2.0                                       | 183.5 ± 4.0                                | 66.3 ± 1.3                    | 26 ± 2                        |
| 1.6                                       | 181                                        | 63                            | 24                            |
| 1.2                                       | 193.6 ± 4.3                                | 64.2 ± 1.4                    | 24.2 ± 1.4                    |
| 0.7                                       | 230.3 ± 2.3                                | 61.0 ± 1.0                    | 21.7 ± 0.4                    |
| 0.49                                      |                                            | 59                            | 17                            |
| 0.2                                       | 221 ± 20                                   | 49.8 ± 1.8                    | 14.7 ± 0.50                   |
| 0.106                                     |                                            | 41.3 ± 1.7                    | 10.3 ± 0.6                    |
| 3.33 × 10 <sup>-3</sup>                   |                                            | 15.6                          | 2.7                           |
| 2.31 × 10 <sup>-3</sup>                   |                                            | 14.9                          | 1.4                           |

<sup>a</sup> Conditions:  $(7.20 \pm 0.02) \times 10^{-3}$  *M* NaClO<sub>2</sub> and 2.0 *M* ionic strength with NaClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> The number following a "±" sign always refers to the average deviation from replicate runs.

presence of initial chloride ion, the rate does depend on the hydrogen ion concentration.

The data in Table II summarize the effect of chloride ion on the disproportionation of chlorous acid. At a hydrogen ion concentration of 1.2 *M*, the rate changes from a half-life of approximately 400 min in the absence of initial chloride ion to a half-life of a few minutes with 0.1 *M* chloride added initially.

TABLE II

EFFECT OF CHLORIDE ION ON THE RATE OF THE REACTION<sup>a</sup> IN 1.2 *M* HClO<sub>4</sub>

| [Cl <sup>-</sup> ], <i>M</i> | <i>t</i> <sub>1/2</sub> , min | <i>t</i> <sub>3/4</sub> , min |
|------------------------------|-------------------------------|-------------------------------|
| 0                            | 389 ± 3                       |                               |
| 6.77 × 10 <sup>-5</sup>      | 397                           |                               |
| 6.77 × 10 <sup>-4</sup>      | 296                           |                               |
| 6.77 × 10 <sup>-3</sup>      | 90.5 ± 1.5                    | 197 ± 9                       |
| 0.01                         | 64.1 ± 1.6                    | 137.4 ± 7.7                   |
| 0.04                         | 17.17 ± 0.43                  | 36.92 ± 0.78                  |
| 0.01 <sup>b</sup>            | 68.5 ± 0.7                    |                               |
| 0.04 <sup>b</sup>            | 18.15 ± 1.85                  | 38.40 ± 0.90                  |
| 0.1 <sup>b</sup>             | 6.85 ± 0.05                   | 14.35 ± 0.05                  |

<sup>a</sup> Conditions:  $(3.60 \pm 0.02) \times 10^{-3}$  *M* NaClO<sub>2</sub> and 2.0 *M* ionic strength with NaClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> Conditions:  $(1.99 \pm 0.01) \times 10^{-3}$  *M* NaClO<sub>2</sub> and 2.0 *M* ionic strength with NaClO<sub>4</sub> at 25 ± 0.5°.

The data in Table III show that the initial concentration of chlorous acid only has an appreciable effect on the rate if the initial concentration of chloride is small. This is also reflected in the order of the reaction with respect to chlorous acid. A compilation of these results is shown in Table IV. In the absence of added chloride ion, the order is approximately 2 with 1.2–2.0 *M* hydrogen ion concentrations. As the added chloride ion concentration increases, the order decreases and approaches 1 at high chloride ion concentrations. An increase of the hydrogen ion concentration to 4.0 *M* with 0.01 *M* added chloride ion results in an order with respect to chlorous acid of 1.0. Thus, at high hydrogen ion concentrations the rate-determining step for the chloride-catalyzed path involves only one chlorous acid molecule.

The effect of ionic strength is to increase the rate of the reaction. For example, with  $7.2 \times 10^{-3}$  *M* NaClO<sub>2</sub> and 2.0 *M* HClO<sub>4</sub> at 25°, a change in the ionic strength from 2.0 to 4.0 *M* results in the half-life<sup>15</sup> decreasing

TABLE III

EFFECT OF THE INITIAL CONCENTRATION OF SODIUM CHLORITE ON THE RATE OF THE REACTION<sup>a</sup>

| 10 <sup>3</sup> [ClO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> , <i>M</i> | <i>t</i> <sub>1/2</sub> , min | 10 <sup>3</sup> [ClO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> , <i>M</i> | <i>t</i> <sub>1/2</sub> , min |
|--------------------------------------------------------------------------|-------------------------------|--------------------------------------------------------------------------|-------------------------------|
| 7.21 ± 0.05 <sup>b</sup>                                                 | 193 ± 4                       | 1.99 ± 0.01 <sup>c</sup>                                                 | 6.85 ± 0.05                   |
| 4.87 ± 0.02 <sup>b</sup>                                                 | 292 ± 12                      | 1.32 <sup>c</sup>                                                        | 7.5                           |
| 3.61 ± 0.03 <sup>b</sup>                                                 | 389 ± 3                       | 0.99 <sup>c</sup>                                                        | 7.6                           |

<sup>a</sup> With 1.2 *M* HClO<sub>4</sub> at an ionic strength of 2.0 *M* with NaClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> No added chloride ion. <sup>c</sup> With 0.10 *M* NaCl added initially.

TABLE IV

ORDER OF THE DISPROPORTIONATION REACTION WITH RESPECT TO CHLOROUS ACID CONCENTRATION<sup>a</sup>

| [H <sup>+</sup> ] <sub>0</sub> , <i>M</i> | [Cl <sup>-</sup> ] <sub>0</sub> , <i>M</i> | <i>n</i> <sub>1/2</sub> <sup>b</sup> | [H <sup>+</sup> ] <sub>0</sub> , <i>M</i> | [Cl <sup>-</sup> ] <sub>0</sub> , <i>M</i> | <i>n</i> <sub>1/2</sub> <sup>b</sup> |
|-------------------------------------------|--------------------------------------------|--------------------------------------|-------------------------------------------|--------------------------------------------|--------------------------------------|
| 0.2                                       |                                            | 1.67                                 | 1.2                                       | 6.8 × 10 <sup>-3</sup>                     | 1.31                                 |
| 2.0                                       |                                            | 1.91                                 | 1.2                                       | 0.01                                       | 1.22                                 |
| 1.2                                       |                                            | 2.01                                 | 1.2                                       | 0.04                                       | 1.20                                 |
| 1.2                                       | 6.8 × 10 <sup>-5</sup>                     | 1.94                                 | 1.2                                       | 0.10                                       | 1.15                                 |
| 1.2                                       | 6.8 × 10 <sup>-4</sup>                     | 1.79                                 |                                           |                                            |                                      |

<sup>a</sup> Conditions:  $(1.0\text{--}7.2) \times 10^{-3}$  *M* NaClO<sub>4</sub> at 2.0 *M* ionic strength with NaClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> The order was determined by means of the Noyes equation

$$n_{1/2} = 1 + \frac{\log t_{1/2} - t'_{1/2}}{\log a' - \log a}$$

where *a* is the initial concentration of sodium chlorite and *t*<sub>1/2</sub> is the time required for half of the initial chlorite to decompose. In 0.2, 1.2, and 2.0 *M* HClO<sub>4</sub> solutions in the absence of chloride ion and with the appropriate quarter- or eighth-lives, values of *n*<sub>1/4</sub> of 1.53, 1.95, and 1.99 and *n*<sub>1/8</sub> of 1.12, 1.80, and 2.02, respectively, were calculated.

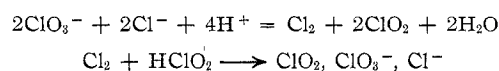
from 184 ± 4 to 120 ± 3 min. (The number following a "±" sign always refers to the average deviation from replicate runs.)

Only semiquantitative experiments were performed in order to determine the effect of temperature on the rate. Above 25° it became more difficult to control the loss of chlorine dioxide but with an initial sodium chlorite concentration of  $7.2 \times 10^{-3}$  *M* and with 1.2 *M* perchloric acid, the half-lives<sup>15</sup> were 194 ± 4, 79 ± 2, and 46 min at 25, 35, and 40°, respectively.

In agreement with the results obtained by Taube and Dodgen<sup>10</sup> and White, Taylor, and Vincent,<sup>12</sup> at low chlorate ion concentrations (comparable to the maximum amount of chlorate ion that could be formed in any of the kinetic runs), we find that chlorate ion had, at most, only a very small effect on the rate of disproportionation of chlorous acid.<sup>16</sup> Chlorine dioxide also was found to have, at most, a very small effect on the rate.

A variety of rate laws were tried in an attempt to fit the experimental data which were obtained under a variety of different conditions to a single mathematical expression. Since the order with respect to chlorous acid appeared to be 2 in the absence of added chloride

(16) High chlorate concentrations, 0.1–0.12 *M*, had an effect on the rate of the reaction. This may be due to an impurity in the sodium chlorate or possibly to the following path



ion and with 1.2 *M* perchloric acid, a second-order rate law was first attempted

$$-\frac{d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 \quad (14)$$

When only the first 25% of the reaction was considered, the deviation from the second-order rate law was less than 1% and  $k_1$  is  $(1.19 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ .

The second-order rate law did not fit the data when chloride ion was present initially and the second-order fits became poorer as the reaction proceeded in that chloride ion is produced during the reaction.<sup>3</sup> Thus, it was necessary to try a more complicated rate law which would take into account the catalytic effect of the chloride ion.

The rate law

$$-\frac{d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + k_2'[\text{HClO}_2][\text{Cl}^-] \quad (15)$$

fits the data at 1.2 *M* hydrogen ion from  $6.77 \times 10^{-3}$  to 0.1 *M* added chloride ion to better than 5% if the value of  $k_1 = 1.19 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  is used. Similarly the equation

$$-\frac{d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + k_2''[\text{HClO}_2][\text{Cl}^-]^2 \quad (16)$$

also fits the data to better than 5%. However, the values of  $k_2'$  and  $k_2''$  are dependent on the initial chloride ion concentration as can be seen from the data in Table V.

TABLE V  
DETERMINATION OF  $k_2$  FROM THE TWO-TERM RATE LAW<sup>a</sup>

| $[\text{Cl}^-]_0, M$    | $k_2'$ from eq 15,<br>$M^{-1} \text{ sec}^{-1}$ | $k_2''$ from eq 16,<br>$M^{-2} \text{ sec}^{-1}$ |
|-------------------------|-------------------------------------------------|--------------------------------------------------|
| $6.77 \times 10^{-3}^b$ | $1.27 \times 10^{-2}$                           | 1.80                                             |
| 0.01 <sup>b</sup>       | $1.42 \times 10^{-2}$                           | 1.40                                             |
| 0.04 <sup>c</sup>       | $1.50 \times 10^{-2}$                           | 0.38                                             |
| 0.1 <sup>d</sup>        | $1.53 \times 10^{-2}$                           | 0.15                                             |

<sup>a</sup> Conditions:  $(1.0-7.2) \times 10^{-3} M$  NaClO<sub>2</sub> and 1.2 *M* HClO<sub>4</sub> at  $25 \pm 0.5^\circ$ . The calculated value of  $k_1$  corresponded to  $(1.19 \pm 0.06) \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  for all of the data shown. <sup>b</sup> Average of eight kinetic runs with an average of  $75 \pm 3\%$  of the reaction completed. <sup>c</sup> Average of ten kinetic runs with an average of  $90 \pm 2\%$  of the reaction completed. <sup>d</sup> Average of four kinetic runs with an average of  $92 \pm 2\%$  of the reaction completed.

A preequilibrium step which involves chlorous acid and chloride ion could account for the deviations found in Table V. Thus, the rate law

$$-\frac{d[\text{HClO}_2]}{dt} = k_1[\text{HClO}_2]^2 + \frac{k_2[\text{HClO}_2][\text{Cl}^-]^2}{K + [\text{Cl}^-]} \quad (17)$$

was tried which reduces to eq 15 at high chloride ion concentrations. Approximate values for  $k_2$  and  $K$  in eq 17 were obtained<sup>17</sup> by plotting  $[\text{Cl}^-]_0/k_2'$  vs.  $[\text{Cl}^-]_0$ .

(17) If the second term in eq 15 is set equal to the second term in eq 17, we obtain

$$k_2'[\text{HClO}_2][\text{Cl}^-] = \frac{k_2[\text{HClO}_2][\text{Cl}^-]^2}{K + [\text{Cl}^-]}$$

Rearranging

$$\frac{[\text{Cl}^-]}{k_2'} = \frac{K}{k_2} + \frac{[\text{Cl}^-]}{k_2}$$

A plot of  $[\text{Cl}^-]_0/k_2'$  vs.  $[\text{Cl}^-]_0$  is linear with a slope of  $1/k_2$  and an intercept of  $K/k_2$ .

By this method it was found that  $k_2$  should be approximately  $1.6 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$  and  $K$  approximately  $1.1 \times 10^{-3}$  if  $k_1$  is  $1.19 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ . For all of the kinetic runs at 1.2 *M* hydrogen ion with  $<10^{-7}$ –0.1 *M* chloride ion added initially, attempts were made to evaluate the parameters for eq 17. A summary of the attempted least-squares fits for various values of the parameters is shown in Table VI. The variation of the fit as measured by the average per cent deviation is given as a function of the chloride ion concentration in Table VII. Somewhat better fits are obtained by varying the individual parameters slightly for each different chloride ion concentration, and these results are shown in Table VIII. However, for 1.2 *M* perchloric acid, the best set of resulting values for  $k_1$ ,  $k_2$ , and  $K$  were  $1.17 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $1.57 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $1.20 \times 10^{-3} M$ , respectively, with an average per cent deviation of the fitted values of 5.3%. These values of  $k_1$ ,  $k_2$ , and  $K$  were used in conjunction with eq 17 to calculate the concentration of chlorite ion as a function of time. A comparison of the experimental and calculated values for two different experiments is given in Tables IX and X. The experimental values agree with the calculated values to better than  $\pm 1\%$  on the average.

TABLE VI  
EFFECT<sup>a</sup> OF VARIOUS VALUES OF  $k_1$ ,  $k_2$ , AND  $K$  ON THE AVERAGE PER CENT DEVIATIONS FOR EQ 17

| $10^2 k_1$ ,<br>$M^{-1}$<br>$\text{sec}^{-1}$ | $10^2 k_2$ ,<br>$M^{-1}$<br>$\text{sec}^{-1}$ | $10^3 K$ ,<br>$M$ | Av<br>% dev | $10^2 k_1$ ,<br>$M^{-1}$<br>$\text{sec}^{-1}$ | $10^2 k_2$ ,<br>$M^{-1}$<br>$\text{sec}^{-1}$ | $10^3 K$ ,<br>$M$ | Av<br>% dev |
|-----------------------------------------------|-----------------------------------------------|-------------------|-------------|-----------------------------------------------|-----------------------------------------------|-------------------|-------------|
| 1.25                                          | 1.57                                          | 1.50              | 6.4         | 1.17                                          | 1.57                                          | 1.50              | 5.5         |
| 1.22                                          | 1.57                                          | 1.50              | 5.9         | 1.17                                          | 1.57                                          | 1.20              | 5.3         |
| 1.22                                          | 1.57                                          | 1.00              | 6.3         | 1.17                                          | 1.57                                          | 1.00              | 5.5         |
| 1.17                                          | 1.53                                          | 1.50              | 5.8         | 1.08                                          | 1.57                                          | 1.50              | 6.6         |
| 1.17                                          | 1.57                                          | 2.00              | 6.2         |                                               |                                               |                   |             |

<sup>a</sup> Conditions:  $(1.0-7.2) \times 10^{-3} M$  NaClO<sub>2</sub>, with 0.0–0.1 *M* NaCl and 1.2 *M* HClO<sub>4</sub> at  $25 \pm 0.5^\circ$  for a total of 46 kinetic runs.

TABLE VII  
AVERAGE PER CENT DEVIATION AS A FUNCTION OF THE CHLORIDE ION CONCENTRATION<sup>a</sup>

| $[\text{Cl}^-]_0, M$ | Av % dev | No. of runs |
|----------------------|----------|-------------|
| 0                    | 5.8      | 11          |
| $6.8 \times 10^{-5}$ | 7.2      | 4           |
| $6.8 \times 10^{-4}$ | 6.2      | 2           |
| $6.8 \times 10^{-3}$ | 3.9      | 8           |
| 0.01                 | 4.1      | 8           |
| 0.04                 | 5.9      | 9           |
| 0.1                  | 5.7      | 4           |

<sup>a</sup> Conditions:  $(1.0-7.2) \times 10^{-3} M$  NaClO<sub>2</sub> and 1.2 *M* HClO<sub>4</sub> at  $25 \pm 0.5^\circ$ . The best fit values of the parameters in eq 17 are  $K = 1.2 \times 10^{-3} M$ ,  $k_1 = 1.17 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $k_2 = 1.57 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ .

With 2.0 *M* perchloric acid, values of  $k_1$ ,  $k_2$ , and  $K$  of  $1.17 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ ,  $3.00 \times 10^{-2} \text{ M}^{-1} \text{ sec}^{-1}$ , and  $1.20 \times 10^{-3} M$ , respectively, are obtained with an average deviation of 4.6%. Apparently,  $k_1$  and  $K$  are independent of the hydrogen ion concentration in the 1.2–2.0 *M* range, and  $k_2$  is directly proportional to the hydrogen ion concentration. These kinetic observations are completely consistent with the stoichiometric

TABLE VIII  
BEST SET OF PARAMETERS FOR A GIVEN INITIAL  
CHLORIDE ION CONCENTRATION<sup>a</sup>

| [Cl <sup>-</sup> ], M   | 10 <sup>3</sup> k <sub>1</sub> ,<br>M <sup>-1</sup> sec <sup>-1</sup> | 10 <sup>3</sup> k <sub>2</sub> ,<br>M <sup>-1</sup> sec <sup>-1</sup> | 10 <sup>3</sup> K,<br>M | Av %<br>dev <sup>b</sup> |
|-------------------------|-----------------------------------------------------------------------|-----------------------------------------------------------------------|-------------------------|--------------------------|
| 0.0                     | 1.17                                                                  | 1.57                                                                  | 2.00                    | 5.6                      |
| 6.77 × 10 <sup>-5</sup> | 1.08                                                                  | 1.57                                                                  | 1.50                    | 4.1                      |
| 6.77 × 10 <sup>-4</sup> | 1.17                                                                  | 1.57                                                                  | 1.00                    | 6.0                      |
| 6.77 × 10 <sup>-3</sup> | 1.22                                                                  | 1.57                                                                  | 1.50                    | 3.5                      |
| 0.01                    | 1.22                                                                  | 1.57                                                                  | 1.00                    | 2.7                      |
| 0.04                    | 1.22                                                                  | 1.57                                                                  | 1.50                    | 5.6                      |
| 0.1                     | 1.22                                                                  | 1.57                                                                  | 1.50                    | 5.5                      |

<sup>a</sup> Conditions: (3.6–7.2) × 10<sup>-3</sup> M NaClO<sub>2</sub> and 1.2 M HClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> The average per cent deviations would be considerably smaller if several runs with exceptionally large deviations were deleted.

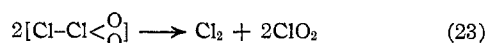
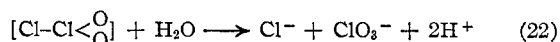
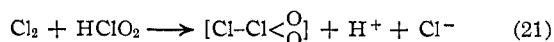
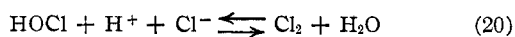
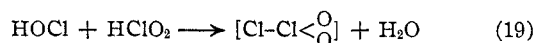
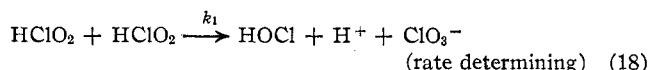
TABLE IX  
COMPARISON OF EXPERIMENTAL AND CALCULATED RATE DATA FOR  
THE DISPROPORTIONATION OF CHLOROUS ACID IN THE ABSENCE OF  
INITIAL CHLORIDE ION<sup>a</sup>

| Time,<br>min | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>obsd</sub> ,<br>M | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>obsd</sub> ,<br>M | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>calcd</sub> , <sup>b</sup><br>M |
|--------------|------------------------------------------------------------|------------------------------------------------------------|--------------------------------------------------------------------------|
| 0.0          | ...                                                        | 3.64                                                       | 3.64                                                                     |
| 9.6          | 0.067                                                      | 3.49                                                       | 3.56                                                                     |
| 14.3         | 0.083                                                      | 3.46                                                       | 3.52                                                                     |
| 49.3         | 0.194                                                      | 3.15                                                       | 3.23                                                                     |
| 77.8         | 0.267                                                      | 3.00                                                       | 3.03                                                                     |
| 108.8        | 0.341                                                      | 2.81                                                       | 2.84                                                                     |
| 136          | 0.399                                                      | 2.68                                                       | 2.69                                                                     |
| 197          | 0.522                                                      | 2.43                                                       | 2.40                                                                     |
| 227          | 0.576                                                      | 2.31                                                       | 2.28                                                                     |
| 293          | 0.684                                                      | 2.11                                                       | 2.04                                                                     |
| 320          | 0.725                                                      | 2.03                                                       | 1.96                                                                     |
| 347          | 0.765                                                      | 1.93                                                       | 1.87                                                                     |
| 408          | 0.845                                                      | 1.79                                                       | 1.72                                                                     |
| 477          | 0.926                                                      | 1.60                                                       | 1.56                                                                     |

<sup>a</sup> With 3.64 × 10<sup>-3</sup> M NaClO<sub>2</sub> and 1.2 M HClO<sub>4</sub> at an ionic strength of 2.0 M with NaClO<sub>4</sub> at 25 ± 0.5°. <sup>b</sup> Calculated on the basis of eq 17 with k<sub>1</sub> = 1.17 × 10<sup>-2</sup> M<sup>-1</sup> sec<sup>-1</sup>, k<sub>2</sub> = 1.57 × 10<sup>-2</sup> M<sup>-1</sup> sec<sup>-1</sup>, and K = 0.0012 M.

observations reported previously.<sup>3</sup> Thus, eq 17 is an accurate (±5%) mathematical representation of the experimental data, and it gives a consistent interpretation of the change of order of the reaction with respect to chlorous acid as a function of chloride and hydrogen ion concentration.

These results can be interpreted in terms of the following: path 1: uncatalyzed



path 2: chloride ion catalyzed

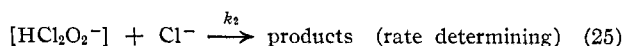


TABLE X  
COMPARISON OF EXPERIMENTAL AND CALCULATED RATE DATA  
FOR THE DISPROPORTIONATION OF CHLOROUS ACID  
IN THE PRESENCE OF 0.01 M CHLORIDE ION<sup>a</sup>

| Time,<br>min | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>obsd</sub> ,<br>M | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>obsd</sub> ,<br>M | 10 <sup>3</sup> [ClO <sub>2</sub> ] <sub>calcd</sub> , <sup>b</sup><br>M |
|--------------|------------------------------------------------------------|------------------------------------------------------------|--------------------------------------------------------------------------|
| 0.0          | 0.0                                                        | 3.61                                                       | 3.61                                                                     |
| 5.1          | 0.146                                                      | 3.45                                                       | 3.42                                                                     |
| 8.5          | 0.242                                                      | 3.33                                                       | 3.29                                                                     |
| 13.3         | 0.370                                                      | 3.14                                                       | 3.13                                                                     |
| 19.2         | 0.518                                                      | 2.94                                                       | 2.94                                                                     |
| 22.5         | 0.589                                                      | 2.81                                                       | 2.84                                                                     |
| 30.0         | 0.750                                                      | 2.60                                                       | 2.62                                                                     |
| 37.3         | 0.890                                                      | 2.45                                                       | 2.44                                                                     |
| 48.2         | 1.083                                                      | 2.18                                                       | 2.19                                                                     |
| 58.8         | 1.242                                                      | 1.96                                                       | 1.98                                                                     |
| 69.0         | 1.378                                                      | 1.80                                                       | 1.80                                                                     |
| 81.0         | 1.518                                                      | 1.56                                                       | 1.61                                                                     |
| 96.0         | 1.660                                                      | 1.36                                                       | 1.42                                                                     |
| 119.7        | 1.841                                                      | 1.12                                                       | 1.17                                                                     |
| 129.7        | 1.906                                                      | 1.06                                                       | 1.08                                                                     |
| 139.7        | 1.961                                                      | 0.95                                                       | 1.01                                                                     |

<sup>a</sup> With 3.61 × 10<sup>-3</sup> M NaClO<sub>2</sub> and 1.2 M HClO<sub>4</sub> at an ionic strength of 2.0 M with NaClO<sub>4</sub> at 25 ± 0.05°. <sup>b</sup> Calculated on the basis of eq 17 with k<sub>1</sub> = 1.17 × 10<sup>-2</sup> M<sup>-1</sup> sec<sup>-1</sup>, k<sub>2</sub> = 1.57 × 10<sup>-2</sup> M<sup>-1</sup> sec<sup>-1</sup>, and K = 0.0012 M.

The value of K<sup>-1</sup> corresponds to 1/K or 833 M<sup>-1</sup> at 25°. No additional details for the formation of products in eq 25 were obtained directly.<sup>3</sup>

An interesting comparison of the proposed [HCl<sub>2</sub>O<sub>2</sub>]<sup>-</sup> intermediate with [Cl<sub>2</sub>O<sub>2</sub>] and [IClO<sub>2</sub>]<sup>-</sup><sup>18</sup> can be made. The [Cl<sub>2</sub>O<sub>2</sub>] intermediate rapidly disproportionates to form ClO<sub>2</sub> and ClO<sub>3</sub><sup>-</sup> depending on the concentration of the intermediate.<sup>19</sup> However, [Cl<sub>2</sub>O<sub>2</sub>] has also been shown to have oxidizing properties in that, for example, phenol<sup>20,21</sup> is more rapidly oxidized by [Cl<sub>2</sub>O<sub>2</sub>] than by HOCl or ClO<sub>2</sub>. The proposed species<sup>18</sup> [IClO<sub>2</sub>]<sup>-</sup> is also reported to undergo primarily internal oxidation-reduction to form I<sup>·</sup> (and ultimately I<sub>2</sub>) and ClO<sub>2</sub><sup>-</sup> rather than to oxidize I<sup>-</sup> or ClO<sub>2</sub><sup>-</sup>. On the other hand, the kinetic evidence offered in this paper suggests that [HCl<sub>2</sub>O<sub>2</sub>]<sup>-</sup> readily oxidizes Cl<sup>-</sup> rather than undergoing other possible redox reactions.

The only other hydrogen ion concentration at which extensive kinetic studies were carried out was 0.2 M acid. At this hydrogen ion concentration eq 17 did not fit the data<sup>22</sup> and the average per cent deviation was about 15%. Attempts to fit the data with more complicated rate laws were also unsuccessful. This greater complexity at low hydrogen ion concentrations is to be expected since evidence has been found for a third path<sup>3</sup> which makes its maximum contribution in the 2–3 pH range. In Figure 1 the absorbance at 3585 Å of a

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(19) F. Emmenegger and G. Gordon, *Inorg. Chem.*, **6**, 633 (1967).

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

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(22) We also find that with 0.2 M perchloric acid relatively less chlorine dioxide and more chlorate ion is produced than at the higher acidities.<sup>3</sup> Furthermore, the initial rate of the reaction is faster with 0.2 M acid than it is with 2.0 M acid. The order with respect to chlorous acid is 2 with 2.0 M acid in the absence of added chloride, but with 0.2 M acid the order with respect to chlorous acid, based on the half-life, is 1.67; the order based on the quarter-life is 1.53 and the order based on the eighth-life is 1.12. This latter observation would seem to indicate that at the beginning of the reaction the rate is first order with respect to chlorous acid concentration.

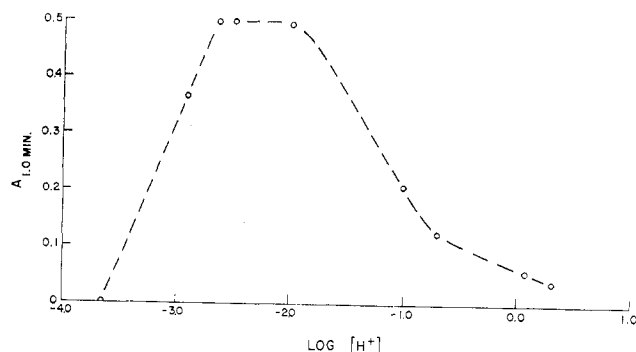


Figure 1.—Formation of chlorine dioxide as a function of the hydrogen ion concentration;  $[\text{ClO}_2^-]_0 = 7.2 \times 10^{-3} M$ ,  $[\text{Cl}^-]_0 = 0$ ; temperature  $25 \pm 0.5^\circ$ ; ionic strength  $2.0 M$ .  $A_{1.0 \text{ min}}$  is absorbance at  $3585 \text{ \AA}$  after 1 min.

$7.2 \times 10^{-3} M$  sodium chlorite solution, after the reaction has proceeded for 1 min ( $A_{1 \text{ min}}$ ), is plotted as a function of the log of the hydrogen ion concentration. The absorbance of the solution, which is proportional to the concentration of chlorine dioxide, increases markedly as the hydrogen ion concentration decreases and reaches a maximum at pH 2.0–2.7 and then decreases rapidly to zero as the hydrogen ion concentration is further decreased. Buser and Hanisch<sup>8</sup> and White, Taylor, and Vincent<sup>12</sup> noted a similar maximum

near pH 2 in the formation of chlorine dioxide from buffered solutions.

The initial rate of formation of chlorine dioxide appears to correspond to the relative amounts of chlorite ion and chlorous acid present;<sup>8</sup> *i.e.*, the maximum production of chlorine dioxide occurs approximately at the  $pK_a$  of chlorous acid<sup>23</sup> ( $pK_a = 2.31$ ). These observations suggest a third term in the rate law which involves the reaction of chlorite ion and chlorous acid to form an intermediate of the composition  $[\text{HClO}_2 \cdot \text{ClO}_2^-]$ . The observations here suggest that the intermediate produces chlorine dioxide more rapidly in the low acid region than does either the first or the second term of the rate law.

More detailed studies must be carried out in order to understand completely the mechanism of the disproportionation of chlorous acid at low hydrogen ion concentrations. Necessarily, only kinetic and stoichiometric studies in buffered solutions should be performed which make the studies somewhat more complicated since most common organic buffers are oxidized by chlorine(III) and chlorine(IV) solutions.<sup>21</sup>

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## The Kinetics and Mechanism of the Oxidation of Water by Silver(II) in Concentrated Nitric Acid Solution

By HENRY N. PO, JAMES H. SWINEHART, AND THOMAS L. ALLEN

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The kinetics of the oxidation of water by silver(II) in  $2.00$ – $6.18 M$   $\text{HNO}_3$  has been studied between  $298.15$  and  $308.15^\circ\text{K}$  under a variety of conditions. Studies at  $[\text{Ag(II)}] > 1 \times 10^{-4} M$  show that the reaction is second order in  $[\text{Ag(II)}]$  and the observed rate law is

$$-d[\text{Ag(II)}]/dt = \frac{k_a[\text{Ag(II)}]^2}{k_b + k_d[\text{Ag(I)}][\text{H}^+]^2} = k_{II}[\text{Ag(II)}]^2$$

At  $6.13$ – $6.17 M$   $\text{HNO}_3$  and  $10^4[\text{AgO}]_0 = 8.33$ – $8.50 M$ ,  $k_{II} = 1.78 M^{-1} \text{sec}^{-1}$  at  $298.15^\circ\text{K}$ . The enthalpy of activation for  $k_{II}$  under these concentration conditions is  $23.0 \pm 0.4 \text{ kcal/mole}$ . The proposed mechanism (reactions 1–5) conforms to the observed rate law. The notation  $[\text{Ag(II)}]$  has been used in place of  $[\text{AgNO}_3^+]$  for simplicity. Studies at  $[\text{Ag(II)}] < 1 \times 10^{-4} M$  show that there is a first-order reaction with the rate law

$$-d[\text{Ag(II)}]/dt = \left\{ \frac{k_e + k_t[\text{Ag(I)}]}{(k_r + k_s[\text{Ag(I)}])(k_m + k_n[\text{H}^+]^2)} \right\} [\text{Ag(II)}] = k_I[\text{Ag(II)}]$$

At the same temperature and concentration conditions  $k_{II}$  was reported  $k_I = (2.38 \pm 0.10) \times 10^{-4} \text{ sec}^{-1}$ . The enthalpy of activation,  $\Delta H_I^\ddagger$ , for  $k_I$  is  $22.3 \pm 0.9 \text{ kcal/mole}$ . The mechanism proposed (reactions 8–15) involves a free-radical reaction.

### Introduction

Our interest in silver(II) chemistry came as a result of an investigation of the silver(I)-catalyzed oxidation of oxalate by peroxodisulfate,<sup>1</sup> where it was postulated that silver(I) undergoes a one-electron oxidation by peroxodisulfate to silver(II).

Since silver(II) is a  $d^9$ -electron system, it is paramagnetic. This has been confirmed by Noyes, Pitzer, and Dunn<sup>2</sup> by magnetic susceptibility measurements on silver(II)–nitric acid solutions. More recently, the electron paramagnetic resonance spectra of frozen acid

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