Kinetics of disproportionation of chlorous acid

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Received December 15, 1967

A mechanism involving HOCl, Cl⁻, ClO₂⁻, and Cl₂ as intermediates is proposed for the disproportionation of chlorous acid. In the absence of chloride, the reaction is controlled by two simultaneous processes, 2HClO₂ → H⁺ + HOCl + ClO₂⁻ and HClO₂ + ClO₂⁻ → HOCl + ClO₃⁻. Chloride has a catalytic effect and an inhibiting effect as well on the formation of chlorine dioxide. The initial reaction rate passes through a minimum at a certain concentration of chloride at low acidities, which can be interpreted by the postulated mechanism. Under chloride catalysis, the reaction is controlled by the process H⁺ + Cl⁻ + HClO₂ → 2HOCl.

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The first kinetic investigation of the disproportionation of chlorous acid was carried out in 1935 by Barnett (1), who showed that the rate of formation of chlorine dioxide varied with the square of the chlorous acid concentration. The second-order rate law was also observed by Launer et al. (2) and Nabar et al. (3). However, in 1954, several authors (4, 5) found that the reaction forming chlorine dioxide was second order with respect to total chlorite concentration rather than the equilibrium concentration of chlorous acid.

If the second-order dependence on the equilibrium concentration of chlorous acid is correct, it would be expected that the reaction order with respect to the equilibrium hydrogen ion concentration is 2. Nevertheless, Stitt et al. (5) found that the order was definitely less than 2. The reaction appeared to be nearer to first order with respect to the equilibrium concentration of hydrogen ions than second order, the numerical values falling between 1.0 and 1.2. Buser and Hänisch (6) found that the formation of chlorine dioxide in dilute chlorite solution is not a simple function of pH. They observed a maximum reaction rate at pH 1.70 for a solution of 3.18 × 10⁻³ M NaClO₂. A similar dependence of the reaction rate on pH was found by Hefti (7).

The published literature about the effect of chloride on the rate of disproportionation of chlorous acid is meager. The catalytic effect of chloride was first observed by Barnett (1), who found that the catalyzed disproportionation reaction was first order with respect to chloride and first order with respect to chlorous acid. He also found that in the presence of chloride and after long standing, the reaction was probably complicated by the chloride-catalyzed decomposition of chlorine dioxide.

Several intermediates have been proposed for the formation of chlorine dioxide from the disproportionation of chlorous acid. These include H₃Cl₂O₄, H₂ClO₃, Cl₂O₃, ClO, HOCl by Barnett (1), and Cl—ClO₂ or Cl—I—Cl—O by Taube and Dodgen (8).

An extensive investigation of the disproportionation of chlorous acid both in the absence and presence of chloride has been carried out in the present work. It is hoped that the mechanism postulated from the experimental results will explain many contradictory observations published in the literature.

The parameters investigated include ionic strength, effect of chlorate, and the reaction order with respect to the concentration of each reactant. All experiments were carried out at 25 °C.

A brief investigation on the reaction between chlorous acid and hypochlorous acid was made in order to justify the postulated mechanism.

Experimental

(a) Reagents

Chlorous acid was prepared by the acidification of sodium chlorite containing 97.8% NaClO₂ with nitric acid in most of the kinetic studies. The equilibrium between chlorous acid and chlorite ions is rapidly established upon acidification. The equilibrium concentration of chlorous acid is calculated from the equation (9)

(1) \[ 2\text{HClO}_2 \rightarrow (a + b + K_a) - [(a + b + K_a)^2 - 4ab]^{1/2}, \]

where \( a \) and \( b \) are respectively the concentrations of nitric acid and sodium chlorite after mixing and \( K_a \) is the dissociation constant of chlorous acid expressed in terms of concentrations. \( K_a \) depends on the ionic strength of the solution, as shown in Fig. 1 (9).

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Fig. 1. Effect of ionic strength on the dissociation constant of HClO₂ in terms of concentrations at 25 °C.

Hypochlorous acid solutions, which were used in some experiments, were prepared by adding excess mercuric oxide to a chlorine solution and distilling off the hypochlorous acid.

(b) Experimental Procedure

Separate solutions of nitric acid and sodium chlorite, either in the absence or presence of added chloride, were contained in volumetric flasks and brought to the reaction temperature by immersion in a thermostat for an hour. The reaction was started by adding 10 ml of nitric acid solution with a pipet into a 10-ml sodium chlorite solution contained in a 25-ml volumetric flask immersed in the thermostat. Zero time was taken when the pipet containing nitric acid solution had half-emptied into the sodium chlorite solution. Immediately after mixing, the flask was shaken vigorously. The reacting solution was filled into a 10-mm glass-stoppered absorption cell after rinsing three times. The cell was wiped with tissue paper and placed in the cell compartment of a Beckman DB spectrophotometer. The reaction was followed by measuring the absorbance of chlorine dioxide produced at 360 μm with an automatic chart recorder. The reaction time was calculated from the speed of the recorder.

The initial rates of reaction were calculated from the slopes of absorbance vs. time curves, obtained from the chart recorder, together with the measured molar absorptivity of chlorine dioxide at 360 μm.

Results and Discussions

(A) Disproportionation in the Absence of Chloride

The disproportionation of chlorous acid in the absence of chloride follows the stoichiometry (1, 3, 9)

\[ 2H^+ + 4ClO^- \rightarrow 2ClO_2 + Cl^- + ClO_3^- + H_2O. \]

(a) Ionic Strength Dependence

The ionic strength of the solution was varied by adding sodium nitrate of analytical reagent grade. It was found that the initial reaction rate is independent of ionic strength.

For an ionic reaction, the rate constant is related to ionic strength by the following expression (10, 11),

\[ \log k_2 = \log k_0 + 1.018z_A z_B I^{1/3}; \]

where \( k_2 \) is the rate constant at ionic strength \( I \), \( k_0 \) is the rate constant at zero ionic strength, and \( z_A, z_B \) are the ionic charges of ions.

The independence of the reaction rate from ionic strength in the disproportionation of chlorous acid leads to the conclusion that at least one of the reactants is an uncharged species of chlorous acid. The stoichiometric equation (eq. [2]) as such represents only the net change of the reaction.

(b) Reaction Orders

If the reaction is assumed to occur as a result of the interactions of the undissociated molecules of chlorous acid, the initial rate equation can be written as

\[ \frac{d(ClO_2)}{dt} = k(HClO_2)^n, \]

where \( n \) is the reaction order with respect to the concentration of chlorous acid, or

\[ \log r_0 = \log k + n \log (HClO_2). \]

A plot of \( \log r_0 \) against \( \log (HClO_2) \) should yield a straight line whose slope is equal to the reaction order.

The reaction is second order with respect to the equilibrium concentration of chlorous acid, as shown in Fig. 2. It is of interest to note that as the acidity is decreased, the observed reaction order with respect to chlorous acid decreases slightly. This can be attributed to the dependence of the rate constant of eq. [4] on hydrogen ion concentration rather than the actual change in the reaction order. This result in conjunction with the fact that the four lines in Fig. 2 do not coincide with one another suggests that a reaction occurs between chlorous acid and chlorite ions in parallel with the bimolecular reaction of...
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3.0
1.4
1.8
2.0
2.2
-LOG (HC102)  

-LOG to 

A 0.970 1.98
B 0.400 1.96
C 0.200 1.95
D 0.098 1.71
LINE HNO3 M SLOPE

Fig. 2. Determination of reaction order with respect to chlorous acid.

The overall reaction is the composite of the two reactions, and its rate can be represented by

\[ r_0 = k(HClO_2)^2 + k'(HClO_2)(ClO_2^-). \]

The equilibrium concentration of chlorite ions can be expressed by

\[ (ClO_2^-) = \frac{K_c(HClO_2)}{(H^+)} . \]

Substitution of eq. [7] into eq. [6] and rearranging gives

\[ \frac{r_0}{(HClO_2)^2} = k + k'K_c(H^+). \]

If \( K_c \) is constant, a plot of \( r_0/(HClO_2)^2 \) against \( 1/(H^+) \) should yield a straight line with an intercept equal to \( k \) and a slope equal to \( k'K_c \). The values of \( k \) and \( k' \) at 25°C, as calculated from Fig. 3, are 0.330 and 1.37 l/(mole)(min), respectively. The line in Fig. 3 levels off slightly at low acidity due to the decrease in the dissociation constant of chlorous acid with ionic strength (Fig. 1).

Equation [6] can also be written as

\[ r_0 = k(HClO_2)^2 + k'(HClO_2)(b - (HClO_2)) \]

where \( b \) is the total concentration of sodium chlorite. Differentiation of eq. [9] with respect to the concentration of chlorous acid gives

\[ \frac{dr_0}{d(HClO_2)} = b k' - 2(k' - k)(HClO_2) \]

and

\[ \frac{d^2r_0}{d(HClO_2)^2} = -2(k' - k). \]

Since \( k' \) is greater than \( k \), the second derivative is negative. It is therefore expected that a plot of the initial reaction rate against the equilibrium concentration of chlorous acid will have a maximum, as observed by Buser and Hänisch (6).

Barnett (1) found that the rate law for the disproportionation of chlorous acid was

\[ r = k(HClO_2)^2 \]

and the value of \( k \) at 25°C was 1.4 l/(mole)(min). His experiments were for conditions of fairly low...
acidity, \((\text{ClO}_2^-) > (\text{HClO}_2)\). In view of the low equilibrium concentrations of chlorous acid investigated by him, the bimolecular reaction of chlorous acid may be neglected, and the rate he measured may be mainly due to the reaction between chlorous acid and chlorite ions. The rate constant for the latter reaction is 1.37 \(\text{mole}(\text{min})\) as determined in the present work. Barnett’s rate law cannot explain why there is a maximum reaction rate at a certain pH.

It was found that at the same equilibrium concentration of \(\text{HClO}_2\), the initial rate due to the reaction of \(\text{HClO}_2\) with \(\text{ClO}_2^-\) is approximately directly proportional to the equilibrium concentration of \(\text{ClO}_2^-\). Thus, this reaction is first order with respect to \(\text{ClO}_2^-\).

The rate law represented by eq. [6] explains the contradictory observations published in the literature. When the concentration of sodium chlorite is in excess, the reaction between \(\text{HClO}_2\) and \(\text{ClO}_2^-\) will be predominant, and the reaction order with respect to \(\text{H}^+\) will be close to 1, as observed by Stitt et al. (5). On the other hand, if the acid used for the acidification of sodium chlorite is in excess, the bimolecular reaction of \(\text{HClO}_2\) will be predominant and the reaction order with respect to total chlorite is close to 2, as observed by Launer et al. (4) and Stitt et al. (5), since most of sodium chlorite is converted to chlorous acid.

(c) Effect of Chlorate

Chlorate and chloride are the coproducts of chlorine dioxide in the disproportionation of chlorous acid. It will be of interest to know the effects of these products on the rate of production of chlorine dioxide.

It was found that the addition of 0.324 \(M\) \(\text{NaClO}_3\) into a solution containing 0.0207 \(M\) \(\text{NaClO}_3\) and 0.0375 \(M\) \(\text{H}_2\text{SO}_4\) only increased the initial reaction rate by approximately 6.7%. This implies that the oxidation of chlorite by chlorate also gives chlorine dioxide, but its reaction rate is smaller than that of the disproportionation of chlorous acid (8). It also implies that chlorate does not have an inhibiting effect on the reaction rate.

(B) Disproportionation in the Presence of Chloride

In the presence of chloride, stoichiometric results (9) are compatible with the following two reactions:

\[ 4\text{H}^+ + 5\text{ClO}_2^- \rightarrow 4\text{ClO}_2 + \text{Cl}^- + 2\text{H}_2\text{O} \]

\[ 3\text{ClO}_2^- \rightarrow \text{Cl}^- + 2\text{ClO}_2^- \]

occurring in conjunction with reaction [2]. The contribution of reaction [13] increases with increasing concentration of chloride. Reaction [14] does not give chlorine dioxide and is responsible for the observed inhibiting effect of chloride.

(a) Ionic Strength Dependence

In the presence of chlorite, the disproportionation of chlorous acid is also independent of ionic strength. Consequently, the reaction is expected to proceed through \(\text{HCl} + \text{HClO}_2\) and/or \(\text{H}^+ + \text{Cl}^- + \text{HClO}_2\) and/or \(\text{HCl} + \text{H}^+ + \text{ClO}_2^-\), in which at least one of the reactants is the uncharged species. However, since \(\text{HCl}\) is a much stronger acid than \(\text{HClO}_2\), the reaction is more likely to proceed through \(\text{H}^+ + \text{Cl}^- + \text{HClO}_2\), which is a third-order reaction. The relationship between the rate constant and ionic strength for a third-order ionic reaction has the same expression as eq. [3].

(b) Effect of Chlorate

In the presence of added chloride, it was found that the addition of sodium chlorate also increases the reaction rate slightly, due to the oxidation of chlorous acid by chlorate to give chlorine dioxide.

(c) Catalytic Effect vs. Inhibiting Effect

In contrast to the relatively simple effect of chlorate the presence of chloride affects the disproportionation of chlorous acid in a complex manner. Figure 4 shows that at low acidities, the initial rate of production of chlorine dioxide passes through a minimum as the concentration of added chloride is increased (curves A and B). At high acidities, however, the minimum reaction rate disappears (curve C).

In view of the fact that a minimum reaction rate occurs as the concentration of chloride is increased, it may be concluded that chloride has a catalytic effect and an inhibiting effect as well on the formation of chlorine dioxide. The overall reaction rate is the summation of these two opposing effects and the uncatalyzed disproportionation of chlorous acid.

The solid lines in Fig. 4 are the experimental initial rates as a function of chloride concentration. The calculated values (see the sections on Treatment of Data and Mechanism) are represented by the broken lines.
(d) Reaction Orders

Figure 4 shows that at high concentrations of chloride, there exists a linear relationship between the initial reaction rate and the concentration of chloride. This suggests that the catalytic disproportionation of chlorous acid is first order with respect to the concentration of chloride.

When the concentrations of nitric acid and sodium chloride are maintained constant, the reaction order with respect to chlorous acid can be determined for the chloride-catalyzed reaction. In Fig. 5, \( r_0 \) denotes the overall initial rate of both the chloride-catalyzed and uncatalyzed reactions, and \( r_0' \) the initial reaction rate of the uncatalyzed reaction calculated from the rate constant already determined. The difference between the two reaction rates, or \( r_0 - r_0' \), represents the initial rate due to the chloride-catalyzed reaction, and has approximately a linear relationship with the equilibrium concentration of chlorous acid. This confirms Barnett's results (1) that the chloride-catalyzed reaction is first order with respect to chlorous acid.

The effect of acidity on the chloride-catalyzed reaction is shown in Fig. 6. At a given concentration of chloride, the variation in the slopes of different curves is a measure of the effect of hydrogen ion concentration. Therefore, the reaction order with respect to \( H^+ \) can be determined from the slopes of different curves at a given concentration of chloride. The concentration of chloride may be taken arbitrarily at any value, but it is better to choose higher values than lower ones, since the catalytic effect of chloride preponderates over the inhibiting effect at high concentrations of chloride. Thus, at \( 3.50 \times 10^{-2} M \) NaCl, the slope of each curve, \( \Delta r_0/\Delta(Cl^-) \), can be estimated from Fig. 6. A plot of \( \log [\Delta r_0/\Delta(Cl^-)] \) against \( \log (H^+) \) gives a straight line with slope equal to 0.962, indicating first order with respect to \( H^+ \) under chloride catalysis.

(e) Treatment of Data

The data on the initial rate of formation of chlorine dioxide in the presence of chloride were found to fit the rather complicated expression

\[
[15] \quad r_0 = (m + nx) \left(1 - \frac{x}{p + qx}\right),
\]

FIG. 4. Effect of chloride as a function of acidity.
TABLE I
The four constants of curves A and B in Fig. 4

<p>| | | | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>m</td>
<td>n</td>
<td>p</td>
<td>q</td>
</tr>
<tr>
<td>Curve A</td>
<td>3.62×10⁻⁴</td>
<td>5.05×10⁻⁴</td>
<td>5.21×10⁻³</td>
<td>3.02 (3.35)</td>
</tr>
<tr>
<td>Curve B</td>
<td>1.65×10⁻⁴</td>
<td>1.62×10⁻³</td>
<td>1.11×10⁻³</td>
<td>2.53 (2.28)</td>
</tr>
</tbody>
</table>

where x is the concentration of chloride and m, n, p, and q are positive constants independent of the concentration of chloride but dependent on the equilibrium concentrations of H⁺, HClO₂, and ClO₂⁻. The function has a minimum provided that np > q

When x = 0, eq. [15] is reduced to \( r_0 = m \), which is the initial reaction rate in the absence of chloride. Other constants of eq. [15] can be calculated by making some approximations. When x is large, \( qx \gg p \) so that p is negligible, and eq. [15] becomes

\[
[16] \quad r_0 = (m + nx) \left(1 - \frac{1}{q}\right),
\]

which is the equation of the straight line extended from high values of x. The intercept and the slope of the line are \( n(1 - (1/q)) \) and \( m(1 - (1/q)) \) respectively. The intercept can be used to calculate \( q \), which in turn can be used to calculate n from the slope. On the other hand, when x is small, \( m \gg nx \), and eq. [15] is reduced to

\[
[17] \quad r_0 = m \left(1 - \frac{x}{p + qx}\right),
\]

which can be rearranged to

\[
[18] \quad \frac{1}{1 - (r_0/m)} = \frac{p}{x} + q.
\]

A plot of \( 1/(1 - (r_0/m)) \) vs. \( 1/x \) should give a straight line with slope equal to \( p \), and intercept equal to \( q \), which can be checked against the value obtained from eq. [16].

The four constants for curves A and B in Fig. 4 as fitted by eq. [15] are given in Table I. The values of q in parentheses are those calculated from eq. [18]. The approximations which have been made to calculate these four constants are justified from the relative values of these constants.

The calculated initial reaction rates for curves A and B are shown by the broken lines of Fig. 4. For curve C the range of the concentrations of chloride investigated does not justify the evaluation of the four constants by the same approximations made for curves A and B. However, the four constants for curve C can be evaluated from the concentrations of H⁺, HClO₂, and ClO₂⁻, and will be dealt with in the section of Mechanism.

(C) Reaction between HClO₂ and HOCl

In the oxidation of chlorous acid by hypochlorous acid, stoichiometric results (9) are compatible with the following two parallel reactions:

\[
[19] \quad \text{HOCl} + 2\text{HClO}_2 \rightarrow 2\text{ClO}_2 + \text{Cl}^- + \text{H}^+ + \text{H}_2\text{O}
\]

\[
[20] \quad \text{HOCI} + \text{HClO}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}^- + \text{ClO}_3^-.
\]

In the absence of nitric acid, the dilute solutions of NaClO₂ and HOCI give measurable reaction rates so that the reaction orders can be determined. It was found that reaction [19] which produces chlorine dioxide is first order with respect to the concentrations of both chlorous acid and hypochlorous acid (9).

Mechanism

From the experimental results obtained, a reaction mechanism for the disproportionation of chlorous acid can be proposed.

(A) Disproportionation in the Absence of Chloride

Three steps are involved in the reaction mechanism:

\[
\text{HClO}_2 \rightarrow \text{H}^+ + \text{HOCl} + \text{ClO}_2^-.
\]

\[
\text{ClO}_2^- + \text{HClO}_2 \rightarrow \text{HOCI} + \text{ClO}_3^-.
\]

\[
\text{HOCI} + \text{HClO}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}^- + \text{ClO}_3^-.
\]

The reaction is initiated by hypochlorous acid produced from the disproportionation of two molecules of chlorous acid or one molecule of chlorous acid with one chloride ion, according to steps 1 and 2 which occur simultaneously. The sequence of reactions is propagated by step 3 to form another intermediate, Cl⁻–ClO₂⁻, which then reacts with chlorous acid to give chlorine...
dioxide according to step 4. The observed stoichiometry, eq. [2], can be obtained by the summation of steps 1, 3, and 4, or 2, 3, and 4.

Using the steady-state hypothesis for the concentrations of the two intermediates, HOCl and Cl—ClO₂, gives

$$\frac{d(\text{ClO}_2)}{dt} = 2k_4(\text{HClO}_2)^2$$
$$+ 2k_4(\text{ClO}_2^-)(\text{HClO}_2),$$

which agrees exactly with the empirical expression (eq. [6]). The same rate expression is obtained if ClO₂⁻ is written instead of HClO₂ in steps 3 and 4.

Steps 1 and 2 are slow processes which control the overall reaction rate. Step 3 has been shown to be fast and of second order, being first order with respect to both HClO₂ and HOCl. Step 4 is also expected to be fast, since it involves the reaction with a reactive intermediate.

Steps 1 and 2 are irreversible, since chlorate does not inhibit the reaction, and the equilibrium constants for these two reactions are as high as $3.78 \times 10^{14}$ and $1.87 \times 10^{17}$ respectively. If step 3 is written in reversible form, it does not make any difference to the derived kinetic law. Step 4 is irreversible, since it was experimentally observed that the absorbance of a mixed solution of chlorine dioxide and chloride does not decrease with time.

Since the controlling steps 1 and 2 involve at least one uncharged molecule as reactants, the reaction is independent of ionic strength.

The possible existence of the intermediate CI—ClO₂, first proposed by Taube and Dodgen (8), may be justified partly by the fact that the congeners of oxygen form similar compounds with chlorine, such as S₂Cl₂, Se₂Cl₂, SCOCl₂, and SeOCl₁. Lenzi (12) demonstrated spectrophotometrically the presence of an intermediate in the chloric–hydrochloric acid reaction, which may be CI—ClO₂. In addition to these, it is reasonable to write Cl—ClO₂ as the product, with water as its coproduct, in the bimolecular reaction between chlorous acid and hypochlorous acid, as shown in step 3.

Strictly speaking, the reaction is not taking place in the absence of chloride even if chloride is not added, since chloride is one of the products. However, as the reaction rates were measured only at the initial stages of the reaction, the concentration of chloride produced would be too low to have any significant effect on the reaction.

(2) Disproportionation in the Presence of Chloride

In addition to those elementary steps cited for the disproportionation of chlorous acid in the absence of chloride, the following steps also occur in the present case.

(step 5) $\text{H}^+ + \text{Cl}^- + \text{HClO}_2 \rightarrow 2\text{HOCl}$

(step 6) $\text{H}^+ + \text{Cl}^- + \text{HOCl} \rightarrow \text{H}_2\text{O} + \text{Cl}_2$

(step 7) $\text{Cl}_2 + \text{HClO}_2 + \text{H}_2\text{O} \rightarrow 3\text{H}^+ + 2\text{Cl}^- + \text{ClO}_3^-$

(step 8) $\text{Cl}_2 + \text{HClO}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^- + \text{ClO}_3^-$

Step 5 is introduced to account for the catalytic effect of chloride, and step 6 for the observed inhibition by chloride. Chlorine produced by step 6 is another intermediate in the present system and reacts with chlorous acid in two different paths, one giving the intermediate CI—ClO₂, which is favorable for the formation of chlorine dioxide and the other giving chloride and chlorate.

The summations of (step 3 + step 4) × 2 + step 5, and step 1 + step 6 + step 7, give respectively the stoichiometric eqs. [13] and [14], both of which occur in parallel with reaction [2].

Steps 5, 6, and 7 are all irreversible, since their equilibrium constants are $1.24 \times 10^{2}$, $2.29 \times 10^{3}$, and $1.34 \times 10^{6}$ respectively. Step 8 is written as irreversible to simplify the rate expression derived from the mechanism.

Applying the steady-state hypothesis again to the concentrations of the three intermediates, HOCl, Cl—ClO₂, and Cl₂, gives the following rate expression:

$$\frac{d(\text{ClO}_2)}{dt} = 2k_4(\text{HClO}_2)^2$$
$$+ 2k_4(\text{ClO}_2^-)(\text{HClO}_2)$$

To visualize the effect of chloride, the following quantities are defined.

$$r_0 = \frac{d(\text{ClO}_2)}{dt}$$

$$m = 2k_4(\text{HClO}_2)^2 + 2k_4(\text{ClO}_2^-)(\text{HClO}_2)$$
TABLE I
Calculations of average rate constants or their ratios at 25 °C

\[ q = 1 + k_8/k_7 \]

<table>
<thead>
<tr>
<th>(10^9(\text{H}^+))</th>
<th>(10^4(\text{HClO}_2))</th>
<th>(k_8)</th>
<th>(10^3k_3(k_7 + k_8)/k_8k_7)</th>
<th>(\text{Eq. [16]})</th>
<th>(\text{Eq. [18]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.22</td>
<td>2.68</td>
<td>0.212</td>
<td>4.32</td>
<td>3.02</td>
<td>(3.35)</td>
</tr>
<tr>
<td>8.04</td>
<td>1.76</td>
<td>0.286</td>
<td>5.11</td>
<td>2.53</td>
<td>(2.28)</td>
</tr>
<tr>
<td>3.59</td>
<td>1.51</td>
<td>0.278</td>
<td>2.10</td>
<td>2.17</td>
<td>(2.30)</td>
</tr>
<tr>
<td>3.16</td>
<td>2.10</td>
<td>0.324</td>
<td>5.26</td>
<td>2.46</td>
<td>(2.46)</td>
</tr>
<tr>
<td>3.47</td>
<td>1.52</td>
<td>0.351</td>
<td>3.52</td>
<td>2.15</td>
<td>(2.14)</td>
</tr>
<tr>
<td>Average</td>
<td>0.290</td>
<td>4.06</td>
<td>2.47</td>
<td>(2.51)</td>
<td></td>
</tr>
</tbody>
</table>

[25] \(n = 4k_5(\text{H}^+)(\text{HClO}_2)\)

[26] \(q = k_3(k_7 + k_8)/k_8k_7(\text{H}^+)\)

[27] \(p = k_3(k_7 + k_8)/k_7\)

[28] \(x = (\text{Cl}^-)\).

The substitution of these definitions into eq. [22] gives

\[ r_0 = (m + nx)(1 - \frac{x}{p + qx}), \]

which is the same as the empirical expression.

The values of \(m\), \(n\), and \(p\) are dependent on the equilibrium concentrations of \(\text{H}^+\), \(\text{HClO}_2\), and \(\text{ClO}_2^-\). However, \(q\) is independent of these concentrations.

The calculated rate constants or their ratios by the method given in the section of Treatment of Data are summarized in Tables II and III. The calculated rate constants \(k_1\) and \(k_2\) are those determined from the reaction in the absence of chloride. The rate constants \(k_1, k_2, k_3,\) and \(k_8\) are second-order rate constants with units of \(1/(\text{ mole})\,(\text{min})\), \(k_7\) is a pseudo second-order rate constant, and \(k_5\) and \(k_6\) are third-order rate constants with units of \(1^2/(\text{mole})^2\,(\text{min})\).

By use of the rate constants or their ratios evaluated, the calculated initial rate of formation of chlorine dioxide as a function of the concentration of chloride at high acidity for curve C in Fig. 4 is shown by the broken line in the same figure.

Conclusion

The proposed reaction mechanism for the disproportionation of chlorous acid in the presence or absence of chloride are in good agreement with the experimental results. Although the calculated reaction rates in the presence of chloride at high acidity are somewhat smaller than the experimental values, the calculated results do show that the minimum in the initial reaction rate gradually disappears as the acidity is increased. This is consistent with the experimental observations.

Acknowledgments

The fellowship presented by Rayonier Canada Ltd. (B.C.) in 1963–1964 and the studentship awarded by the National Research Council of Canada in 1964–1966 to C. C. Hong are gratefully acknowledged.