Variation in ClO$_2$/Cl$_2$ Ratio in the Chloride-Chlorate Process under Different Conditions

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Abstract: The chloride-chlorate process is a highly efficient, easy to operate, and cost effective tool for generating ClO$_2$, wherein the theoretical ClO$_2$/Cl$_2$ (γ) ratio is 2. The present study attempts to investigate the optimal conditions for the best reaction yield in terms of chlorine dioxide production and minimal contamination of chlorine. The effects of the molar concentration of sulfuric acid, the temperature, and the chlorate/chloride (Φ) ratio on the ClO$_2$/Cl$_2$ (γ) ratio is examined. The experimental γ-value ranged from 0.46 to as high as 3.4 under different conditions. A reaction mechanism compatible with the experimental observations is proposed, and the role that side reactions have on influencing the ClO$_2$/Cl$_2$ ratio is highlighted. A general equation is derived to express the ClO$_2$/Cl$_2$ ratio.

Keywords: ClO$_2$/Cl$_2$ Ratio, Chlorate/Chloride Ratio, Side Reaction, Mechanism

Introduction

There is growing concern that a simpler, easier to operate, more efficient, and economical technique must be developed for the generation of chlorine dioxide. Chlorine dioxide has achieved a remarkable degree of commercial attention not only because of environmental concerns but also its wide applications in the fields of bleaching, oxidation, and disinfection. It is commercially used in textile, paper, fat, and pulp bleaching, waste water treatment, water purification, removal of phenols from industrial wastes, medical treatment, sanitation, food processing, and aquiculture. The chlorine dioxide-based bleaching process, so-called ECF technology, has become more dominant in the production of bleached chemical pulps [1].

Chlorine dioxide is always generated on-site because of its unstable nature and the risk of its rapid decomposition. In all processes, it is produced from acid solutions of either sodium chlorite or sodium chlorate. Most small and medium scale generators use sodium chlorite as the precursor material particularly for water treatment and disinfection applications because they because require high purity (i.e., Cl$_2$ free) waters. Other applications, which need large quantities of chlorine dioxide, utilize sodium chlorate as the raw material. Economic considerations for the ClO$_2$ generation also play a vital role in the selection of the raw material.

Chlorine dioxide can be generated by reduction of sodium chlorate in relatively concentrated acid solution using various reducing agents, such as sulfur dioxide, methanol, oxalic acid, sodium chlorite, hydrochloric acid, or hydrogen peroxide. The choice of reducing agents is influenced by the operating conditions, the reaction byproducts, and economics of the process.

In the Mathieson process [2-4], an SO$_2$-air mixture is diffused into a solution of sodium chlorate and sulfuric acid. The main stoichiometry of the reaction is represented as:

$$2\text{NaClO}_3 + \text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{ClO}_2 + 2\text{NaHSO}_4$$  \hspace{1cm} (1)

This process yields chlorine dioxide with a much lower content of chlorine, but in low yield and efficiency that are due to several competing side reactions.

The Solvay and R-8 processes [5-8] use sodium chlorate and sulfuric acid with methanol as reducing agent. Complete oxidation of methanol leads its efficient utilization, described by the stoichiometry:
6NaClO₃ + CH₃OH + 4H₂SO₄ → 6ClO₂ + CO₂ + 2Na₃H(SO₄)₂ + 5H₂O \hspace{1cm} (2)

The methanol-chlorate process does not produce chlorine but it has several shortcomings [7-10]. The major drawback of this process is the incomplete oxidation of methanol to formic acid:

12NaClO₃ + 3CH₃OH + 8H₂SO₄ → 12ClO₂ + 3HCOOH + 4Na₃H(SO₄)₂ + 9H₂O \hspace{1cm} (3)

Thus, the overall process stoichiometry of the methanol-chlorate process can be described by the combination of Equations (2) and (3).

Hydrogen peroxide [10-12] is another reducing agent that can produce chlorine dioxide efficiently from acidic sodium chlorate without contamination. The reaction stoichiometry is represented by:

2NaClO₃ + H₂O₂ + H₂SO₄ → 2ClO₂ + O₂ + Na₂SO₄ + 2H₂O \hspace{1cm} (4)

This process has faster reaction kinetics. Hydrogen peroxide is not only quite expensive when compared to other conventional reducing agents but also it is quite unstable; it decomposes rapidly during the course of the reaction, particularly at higher temperatures.

Until now, most chlorine dioxide has been produced by reducing chlorate with sodium chloride, because most pulp bleaching processes still make use of mixtures of chlorine and chlorine dioxide. The proposed stoichiometry of the main reaction [13-17] is:

2NaClO₃ + 2NaCl + 2H₂SO₄ → 2ClO₂ + Cl₂ + 2Na₂SO₄ + 2H₂O \hspace{1cm} (5)

Theoretically, this process gives euchlorine, which is a mixture of chlorine dioxide and chlorine in molar ratio of 2:1. This process gives the highest yield of ClO₂ at the lowest cost among all of the commercial processes. It is simple to operate and responds immediately. The reaction kinetics and mechanism of this process have been discussed by us previously [18]. This present study was aimed at investigating the role of temperature, acid strength, and chlorate/chloride ratio on the ClO₂/Cl₂ ratio. Although it is impossible to produce chlorine-free chlorine dioxide because of the essential presence of chlorine in all chlorate-based ClO₂ generation processes, if the chlorine contamination can be minimized in some way, then this process will be more promising for ClO₂ generation. This work will also be useful in allowing the rational use of resources and to enhance the production of chlorine dioxide under optimized conditions.

**Experimental Section**

The experimental system used for the kinetic study is shown in Figure 1. It is composed of a reactor and an absorber. The reactor is a well-stirred sealed vessel having a total volume of 2.5 L. Continuous stirring is provided by a mechanical agitator. The temperature of the reaction vessel is controlled by a water thermostat (WBC-1506D, JEIO TECH, Korea) to within 0.1°C. Nitrogen gas was purged through the reaction mixture using a bubbling device at a flow rate of 2 L/min. We confirmed that bubbling N₂, which is not pre-saturated with water vapors, has no noticeable effect on the concentration of the reaction solution. The flow rate of
the carrier gas was controlled by using a gas flow meter (KOJIMA-KOFLOC, Japan). The volume of the reaction solution used in each experiment was 1.5 L, which involved sodium chlorate, sodium chloride, and sulfuric acid. The absorber (2 L vessel) consisted of a ca. 2% carbonate-buffered potassium iodide solution. The volume of the absorbing solution was also 1.5 L. Samples from the reactor and absorber were titrated iodometrically or argentometrically using a auto-titrator (Metrohm-Swiss). The potentiometric titration system included a 670 titroprocessor, 730 sample changer, 665 dosimat, and a platinum electrode.

Analytical grade reagents and distilled de-ionized water were used throughout. Sodium chlorate (Aldrich- USA) stock solutions were freshly prepared prior to each experiment and the reactor was wrapped with aluminum foil to avoid the photo-dissociation of chlorine dioxide. The concentration of sulfuric acid was determined by titrating against standard sodium hydroxide using pH meter in each experiment prior to the addition of the salts. Quantitation of the samples from the absorber was analyzed iodometrically [19] against standard NTS solutions. The chlorine dioxide and chlorite concentrations were determined and calculated on the basis of the titration results obtained at neutral (pH ≥ 7) and acidic (pH < 2) conditions. Quantitation of sodium chlorate (Aldrich- USA) consumed in the reactor was determined argentometrically [20] against standard silver nitrate solution, while chlorite concentrations were obtained iodometrically [21] against standard NTS solutions. The precision of these methods was found, to be > 2%. Solutions of NTS (Shinno Pure Chemicals, Japan) and silver nitrate (Kojima-Japan) were prepared and standardized according to standard procedures.

Results and Discussion

To investigate the optimal conditions for the best reaction yield, in terms of chlorine dioxide production and minimal contamination by chlorine, the experiments were carried at different temperatures (25~45°C), chloride/chlorite ratios (0.05~20), and concentrations of sodium chlorate (5.11~200.04 mmol/L), sodium chloride (4.90~150.02 mmol/L), and sulfuric acid (8.51~15.19 N). The kinetic data are reported in Table 1.

The chloride-chlorate reaction, shown in Equation (5), is the basis of the R-2 process for chlorine dioxide generation. It is extremely simple to operate and highly cost effective. According to the main stoichiometry of the reaction, the ClO₂/Cl₂ (η) ratio is equal to 2, but it is variable depending on the reaction conditions. Until now, no reports investigating the reaction conditions responsible for enhanced ClO₂/Cl₂ ratio have been published.

![Figure 2. Effect of temperature on ClO₂/Cl₂ ratio at a chlorate/chloride ratio of ~20 in 9.59 N acid.](image)

Hence, the effect of the various factors on the ClO₂/Cl₂ ratio was the major purpose of the present study.

Effect of Temperature

Keeping chlorate/chloride ratio at ca. 20, experiments were carried out at temperatures of 25, 35, and 45°C in 9.59 N acid. (η)-Values were plotted against temperature and are presented in Figure 2. The data reveal that the ClO₂/Cl₂ ratio is not influenced by temperature at all. It is noteworthy that the η-data in all cases represent the average of three values, which were measured after fixed time intervals upon achieving the steady state.

Effect of Concentration of Acid

The effect of the concentration of sulfuric acid on the ClO₂/Cl₂ ratio was examined by performing experiments at 35°C using different chlorate/chloride ratios, and varying the concentration of sulfuric acid. At a chlorate/chloride ratio of 0.05, the η-value was quite low, i.e., ca. 0.5, and no significant improvement occurred upon increasing the acid concentration from 8.51 to 10.13 N. Similar experiments were carried out at chlorate/chloride ratios of nearly 1 and 20. Although the η-value differed at different chlorate/chloride ratios, the ClO₂/Cl₂ ratio remained unaffected by variations in the acid strength. A graph plotted from the ClO₂/Cl₂ ratio and the concentration of acid at chlorate/chloride ratios of 0.05, 1 and 20 is presented in Figure 3.

Simultaneous Effect of Temperature and Concentration of Acid

In another set of experiments, the temperature and concentration of acid were changed simultaneously at a fixed chlorate/chloride ratio of ca. 1 to examine the combined effect of both factors. Figure 4 depicts the plot of ClO₂/Cl₂ ratio versus temperature at various acid strengths. The ratio was unaffected.
Figure 3. Effect of the concentration of acid on the ClO$_3^-$/Cl$_2$ ratio at different chlorate/chloride ratios.

Figure 4. Combined effects of temperature and acid strength on the ClO$_3^-$/Cl$_2$ ratio at a constant chlorate/chloride ratio ca. 1.

Effect of Chlorate/Chloride Ratio

Experiments were performed at 35°C by varying the chlorate/chloride ratio from 0.05 to 20.43 at different concentration of acid, as shown in Table 1. The data reflect the major role that the chlorate/chloride ratio (ψ) has on influencing the ClO$_3^-$/Cl$_2$ ratio (η). The graph plotted between the η and ψ-values is presented in Figure 5.

At a chlorate/chloride ratio of 0.54, the reaction followed the main stoichiometry with no side reaction, yielding a ClO$_3^-$/Cl$_2$ ratio of ca. 2. When the ψ-value decreased to 0.05, the η-value also reduced to ca. 0.5 because the production of Cl$_2$ was enhanced by the occurrence of the following side reaction [16-18,22] whose kinetics and mechanism have been reported elsewhere [8,22,23]:

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ClO₃⁻ + 5Cl⁻ + 6H⁺ → 3Cl₂ + 3H₂O  \hspace{1cm} (6)

When the chlorate/chloride ratio was ≥ 1, the ClO₃⁻/Cl₂ ratio exceeded 2 and touched a maximum of ca. 3.4 at a \( \Phi \)-value of 4. Thereafter, the ClO₃⁻/Cl₂ ratio decreased slightly as the \( \Phi \)-value increased and attained a steady state. The enhancement in the ClO₃⁻/Cl₂ ratio may be due to the following side reactions:

\[
2\text{HClO}_3 + \text{Cl}_2 + 2\text{H}^+ \rightarrow 2\text{HCl} + 2\text{ClO}_2 \hspace{1cm} (7)
\]
\[
\text{HClO} + 2\text{HClO}_3 \rightarrow 2\text{ClO}_2 + \text{HCl} + \text{H}_2\text{O} \hspace{1cm} (8)
\]

Herein, clorous acid is formed as an intermediate in the main chlorite-chlorate reaction. It can react with chlorite [22], hypochlorite, and chlorine [24-26], or be decomposed in the acidic medium [27-28] to produce chlorine dioxide. The hypochlorite-clorite reaction and acidic decomposition of clorous acid have quite slow reaction kinetics [25] when compared to the chlorine-clorite reaction; furthermore, formation of hypochlorite is favored only by high chloride concentration, so Equation (8) does not contribute much to the enhancement of the ClO₃⁻/Cl₂ ratio at high chloride/chlorite ratios. The chlorine-clorite reaction seems to play a key role in increasing the ClO₃⁻/Cl₂ ratio. It not only consumes the Cl₂ but it also produces more ClO₂ gas and chloride ions from it.

**Proposed Mechanism**

In the light of the discussion above, the chloride-chlorate reaction seems to have the following mechanism. The main stoichiometry of the chlorite-chlorate reaction can be expressed in terms of steps (1) and (2) as follows:

**Step (1)** 3H⁺ + 2Cl⁻ + ClO₃⁻ \( \xrightleftharpoons{\text{k}_1} \) Cl₂+HClO₂+H₂O

**Step (2)** H⁺ + HClO₂ + ClO₃⁻ \( \xleftarrow{\text{k}_2} \) 2ClO₂+H₂O

In the presence of excess chloride (i.e., low chloride/chlorite ratio), the production of Cl₂ is enhanced by the side reaction represented by Equation (6), which is a combination of steps (3) and (4):

**Step (3)** H⁺ + Cl⁻ + HClO₂ \( \xrightarrow{\text{k}_3} \) 2HOCI

**Step (4)** H⁺ + Cl⁻ + HOCI \( \xrightarrow{\text{k}_4} \) Cl₂ + H₂O

In the presence of excess chlorate (i.e., high chloride/chlorite ratio), a portion of Cl₂ is used in situ to generate more ClO₂, as proposed in the side reaction represented by Equation (7), which is combination of steps (5) and (6).

**Step (5)** Cl₂ + HClO₂ \( \xrightarrow{\text{k}_5} \) Cl₂O₂ + HCl

**Step (6)** 2Cl₂O₂ \( \xrightarrow{\text{k}_6} \) Cl₂ + 2ClO₂

The rate of formation of ClO₂ derived from steps (2) and (6) can be expressed as:

\[
\frac{d[\text{ClO}_2]}{dt} = 2k_3[H^+][\text{ClO}_3^-][\text{HClO}_2] + 2k_6[\text{Cl}_2\text{O}_2]^2 \hspace{1cm} (9)
\]

Applying the steady state hypothesis to the concentration of intermediate ClO₂ from steps (5) and (6):

\[
\frac{d[\text{ClO}_2]}{dt} = 0 = k_5[\text{Cl}_2][\text{HClO}_2]-k_6[\text{Cl}_2\text{O}_2]^2 \hspace{1cm} (10)
\]

Thus, the rate of formation of chlorine dioxide can be written as:

\[
\frac{d[\text{ClO}_2]}{dt} = 2[H\text{ClO}_2][k_2[H^+][\text{ClO}_3^-] + k_5[\text{Cl}_2]] \hspace{1cm} (11)
\]

Similarly, applying the steady state hypothesis to the concentration of intermediate HOC_1 from steps (4) and (5):

\[
\frac{d[\text{HOCl}]}{dt} = 0 = 2k_3[H^+][CT][\text{HClO}_2]-k_9[\text{HOCl}][H^+][CT] \hspace{1cm} (12)
\]

Now the rate formation of Cl₂ from steps (1), (3-5), and (6) can be expressed as:

\[
\frac{d[\text{Cl}_2]}{dt} = k_1[H^+][CT][\text{ClO}_3^-]-k_1[\text{Cl}_2][\text{HClO}_2]+k_4

[HOC_1][H^+][CT]-k_5[\text{Cl}_2][\text{HClO}_2]+k_6[\text{Cl}_2\text{O}_2]^2 \hspace{1cm} (13)
\]

Rearranging Equation (13) in the light of Equations (10) and (12), it becomes:

\[
\frac{d[\text{Cl}_2]}{dt} = k_1[H^+][CT][\text{ClO}_3^-][\text{HClO}_2]-k_1[\text{Cl}_2]+2k_5[H^+][CT] \hspace{1cm} (14)
\]

The steady state concentration of chlorous acid [HClO₂] from steps (1-3) and (5) can be expressed as:

\[
[\text{HClO}_2] = \frac{k_5[H^+][CT][\text{ClO}_3^-]}{k_1[\text{Cl}_2]+k_9[H^+][\text{ClO}_2]+k_9[H^+][CT]+k_1[\text{Cl}_2]} \hspace{1cm} (15)
\]

The ratio of the rates of formation of chlorine dioxide and chlorine can be obtained by dividing Equation (11) by Equation (14):
At time $t = 0$, $[\text{ClO}_2] = [\text{Cl}_2] = 0$ and the integration constant for integrated Equation (16) is also zero, so the ratios of rates is equal to the ratios of concentrations. Dividing the numerator and denominator by $[\text{HClO}_3]$, Equation (16) becomes:

$$\frac{[\text{ClO}_2]}{[\text{Cl}_2]} = \frac{\frac{2k_2[H^+][\text{ClO}_3^-] + k_3[\text{Cl}_2]}{[\text{HClO}_3]} - k_1[\text{Cl}_2] + 2k_2[H^+][\text{ClO}_3^-]}{[\text{HClO}_3][\text{Cl}_2]}$$

(17)

Plugging in the value of $[\text{HClO}_3]$ from Equation (15) and solving, Equation (17) becomes:

$$\frac{[\text{ClO}_2]}{[\text{Cl}_2]} = \frac{2k_2[H^+][\text{ClO}_3^-] + k_3[\text{Cl}_2]}{k_2[H^+][\text{ClO}_3^-] + k_2[\text{Cl}_2] + 3k_3[H^+][\text{ClO}_3^-]}$$

(18)

At a low chlorate/chloride ratio (high chloride concentration), there is a significant contribution of Equation (6), which is a combination of steps (3) and (4). Thus, neglecting the term $k_4[\text{Cl}_2]$, the $[\text{ClO}_2]/[\text{Cl}_2]$ ratio reduces to:

$$\frac{[\text{ClO}_2]}{[\text{Cl}_2]} = \frac{2k_2[\text{ClO}_3^-]}{k_2[\text{ClO}_3^-] + 3k_3[H^+][\text{ClO}_3^-]}$$

(19)

The term $k_3[\text{Cl}]$ in the denominator increases upon increasing the chloride concentration. The prediction from Equation (19) that the $\text{ClO}_2/\text{Cl}_2$ ratio will decrease with a decrease in the chlorate/chloride ratio (high chloride concentration) is in agreement with the experimental results.

At a high chlorate/chloride ratio (high chlorate concentration), the $\text{Cl}_2$ produced in step (1) reacts with chlorous acid according to Equation (7). Under this condition, neglecting the $3k_3[H^+][\text{Cl}]$ term in the denominator, the $\text{ClO}_2/\text{Cl}_2$ ratio becomes:

$$\frac{[\text{ClO}_2]}{[\text{Cl}_2]} = \frac{2k_2[H^+][\text{ClO}_3^-] + k_3[\text{Cl}_2]}{k_2[H^+][\text{ClO}_3^-] + k_4[\text{Cl}_2]}$$

(20)

Figure 5 shows a maximum at a chlorate/chloride ratio of about 4 and thereafter the $\text{ClO}_2/\text{Cl}_2$ ratio decreases. This phenomenon is in agreement with the predictions of Equation (20), because a higher chlorate concentration will favor step (2), but it would not enhance the contribution of step (5) by much. Step (5) involves $\text{Cl}_2$ and $\text{HClO}_3$, which are formed slowly in a reversible step (1). As the $\text{ClO}_3^-$ concentration is increased, the contribution of the term $k_4[\text{ClO}_3^-]$ becomes more pronounced relative to $k_3[\text{Cl}_2]$, so the $\text{ClO}_2/\text{Cl}_2$ ratio decreases after a certain specific chloride concentration.

**Conclusions**

Briefly, we conclude that the $\eta$-value is not affected at all by the temperature or the concentration of acid, but the optimum concentration of acid is affected indirectly by the chlorate/chloride ratio. The sole factor responsible for enhancing the $\text{ClO}_2/\text{Cl}_2$ ratio is the chlorate/chloride ratio. The optimum chlorate/chloride molar ratio for a maximum $\text{ClO}_2/\text{Cl}_2$ ratio ranges from 2 to 4. A general equation, which explains the variation in $\text{ClO}_2/\text{Cl}_2$ ratio with chlorate/chloride ratio, is:

$$\frac{[\text{ClO}_2]}{[\text{Cl}_2]} = \frac{2k_2[H^+][\text{ClO}_3^-] + k_3[\text{Cl}_2]}{k_2[H^+][\text{ClO}_3^-] + k_4[\text{Cl}_2] + 3k_3[H^+][\text{ClO}_3^-]}$$

This equation is applicable to both high and low chlorate/chloride ratios.

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