

Kinetics and mechanism of chloride based chlorine dioxide generation process from acidic sodium chlorate

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Abstract

The reaction between sodium chlorate and sodium chloride in presence of aqueous sulfuric acid is studied in a well stirred reactor at various temperatures and molar concentrations of chlorate, chloride and acid. The reaction rate is evaluated by analyzing the consumption of chlorate or chloride iodometrically or argentometrically. The rate law is established. Reaction has been found first and second order with respect to chlorate and chloride concentration, respectively. Reaction order is found about 13–14 with respect to molar concentration of sulfuric acid but it reduced to 2.4 when acidity function, h_{-} , is substituted in place of molar concentration. The temperature dependence of the reaction is also investigated and pre-exponential Arrhenius parameter as well as activation energy are determined. It has been observed that ClO_2/Cl_2 ratio is markedly affected by chlorate to chloride ratio. Reaction mechanism compatible with the reaction kinetics is proposed.

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Keywords: Sodium chlorate; Chlorine-dioxide; Kinetics; Acidity function; Mechanism

1. Introduction

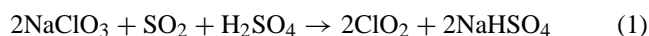
Because of environmental concern, chlorine dioxide has achieved significant commercial attention in the field of pulp bleaching, water purification, fat bleaching, removing phenols from industrial wastes and textile bleaching. Wood pulp bleaching is the prime use of chlorine dioxide as it is a unique selective oxidizer for lignin. Unlike other oxidizing agents, chlorine dioxide does not attack cellulose, and thus preserves the mechanical properties of the bleached pulp. Furthermore, chlorine dioxide functions via oxidation instead of chlorination hence it avoids the formation of chlorinated organic compounds.

In industrial and municipal waste water treatment, chlorine dioxide is quite effective as a biocide over the wide pH range. It helps in eliminating taste and odor problems from drinking waters as it does not react with organic matter to form trihalomethanes (THMs). Chlorine dioxide has also been widely used in many fields such as medical treatment, sanitation, food processing and aquaculture.

It is a powerful oxidizer, quite unstable and cannot be conveniently transported or stored over long periods. It is always generated on site because of its risk of rapid decomposition. In all processes, chlorine dioxide is generated from acid solutions of either sodium chlorite or sodium chlorate. Small and medium scale industrial productions of it utilize sodium chlorite as the raw material particularly for water treatment and disinfection applications as they require high purity (i.e. chlorine free) waters. Other applications, particularly which need large quantities of chlorine dioxide like pulp bleaching, utilize sodium chlorate.

Chlorine dioxide can be generated by reacting sodium chlorate in relatively concentrated acid solution with a reducing agent such as sulfur dioxide, methanol, oxalic acid, hydrogen peroxide, hydrochloric acid or sodium chloride etc. The choice of reducing agent has been influenced by the economics, ease of operation of the process and the environmental concern over the byproducts.

In Mathieson process [1–3], a SO_2 -air mixture is diffused into a aqueous solution of sodium chlorate and sulfuric acid. The main stoichiometry of the reaction is represented as:



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Nomenclature

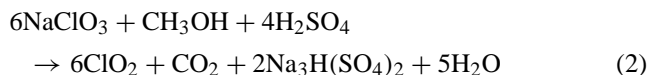
A	pre-exponential Arrhenius parameter
C	constant ($S \times 2.303/2$)
dx/dt	reaction rate
E_a	activation energy (J/mol)
h_-	acidity function
$[H_2SO_4]$	concentration of sulfuric acid (mol/L)
k	rate constant
NTS	sodium thiosulfate
$[NaClO_3]$	concentration of sodium chlorate (mmol/L)
$[NaCl]$	concentration of sodium chloride (mmol/L)
R	gas constant ($8.314 J K^{-1} mol^{-1}$)
S	slope of the straight line during the kinetic plot
T	temperature (K)
t	time (min)

Greek letters

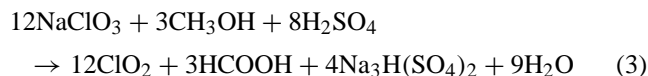
α, β, γ	reaction orders with respect to chlorate, chloride and sulfuric acid
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It yields chlorine dioxide with much lower content of chlorine. This process is slow and has low yield in terms of chlorine dioxide due to several competing side reactions. It needs relatively more concentrated acid solution and higher SO_2 (10–12%) concentrations for the desired reaction rate. Under such conditions, chlorine dioxide is also vulnerable to sulfur dioxide contamination.

The Solvay and R8 process [4–7] use sodium chlorate and sulfuric acid, with methanol as reducing agent. Complete oxidation of methanol leads to efficient utilization of methanol, described by the stoichiometry:



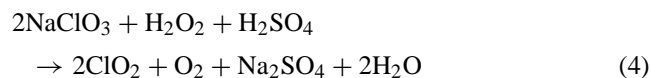
Though methanol-chlorate process does not produce chlorine yet it has several other shortcomings. Firstly, chlorate oxidizes methanol in a stepwise manner, first forming formaldehyde, then formic acid, and finally carbon dioxide. The oxidation of formic acid to carbon dioxide is very slow step [8] so it does not react easily rather volatilize and escape along with highly volatile methyl formate and chlorine dioxide. The incomplete oxidation of methanol to formic acid [6,7,9] is represented as:



So the overall process stoichiometry of methanol-chlorate process can be described by the combination of Eqs. (2) and (3). Secondly, it requires high sulfuric acid concen-

trations to achieve the desired production rate of chlorine dioxide, which results to the formation of acid salt cake. Thirdly, when ClO_2 product is used in bleaching; the unreacted methanol constitutes a pollution load to final user's secondary effluent treatment system. Fourthly, methanol is a combustible and hazardous substance for the workplace.

Hydrogen peroxide [9–11] is another reducing agent, which can efficiently produce chlorine dioxide from chlorate without contaminating it. The reaction stoichiometry is represented as:



This process has faster reaction kinetics. Hydrogen peroxide is not only quite expensive as compared to other conventional reducing agents but also quite unstable and it decomposes rapidly during the course of reaction, particularly at higher temperatures. All these drawbacks in the traditional processes have attracted the attention to advance our research in this field.

Until recently, most of chlorine dioxide was produced by reducing chlorate using sodium chloride. Though it yields chlorine as a major byproduct yet it is quite popular because most of pulp bleaching processes still makes use of mixture of chlorine and chlorine dioxide. This process has fast reaction kinetics and it would be more advantageous for chlorine dioxide generation if anyhow chlorine contamination can be reduced. Though it is unavoidable to produce chlorine free chlorine dioxide due to essential presence of chloride yet it seems possible to minimize the chlorine production. The present study is aimed to study the kinetics and mechanism of the reaction between chlorate and chloride in aqueous sulfuric acid, so that this knowledge can be utilized to make rational use of resources, enhance the production of chlorine dioxide under optimized conditions.

2. Materials and methods

The experimental system used for the kinetic study is shown in Fig. 1. It is composed of a reactor and an absorber. Reactor is well stirred sealed vessel having total volume of 2.5 L. Continuous stirring is provided by a mechanical agitator. Temperature of the reaction vessel is controlled by water thermostat (WBC-1506D, JEIO TECH, Korea) within $\pm 0.1^\circ C$. Nitrogen gas was purged through the reaction mixture using a bubbling device at a flow rate of 2 L/min. It was confirmed that bubbling N_2 , which is not pre-saturated with water vapors has no noticeable effect on the concentration of reaction solution. The carrier gas flow rate was controlled by gas flow meter (KOJIMA-KOFLOC, Japan). The total reaction solution volume taken in each experiment was 1.5 L, which involved sodium chlorate, sodium chloride and sulfuric acid. The absorber (2 L vessel) consisted of ca. 2% carbonate buffered potassium iodide solution. The volume

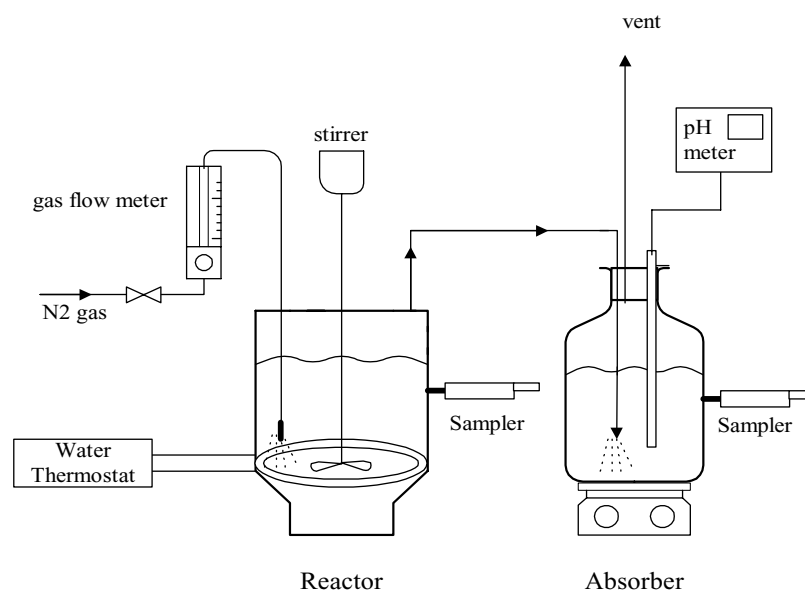


Fig. 1. A schematic diagram of experimental system.

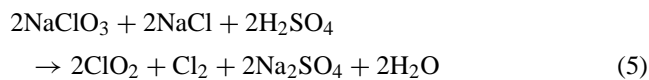
of absorbing solution was also taken 1.5 L. Samples from reactor and absorber were titrated iodometrically or argentometrically using auto-titrator (Metrohm-Swiss). The potentiometric titration system included a 670 titroprocessor, 730 sample changer, 665 dosimat and platinum electrode.

The analytical grade reagents and distilled de-ionized water were used throughout. Sodium chlorate (Aldrich, USA) stock solutions were prepared freshly prior to each experiment and reactor was wrapped with an aluminium foil to avoid the photo-dissociation of chlorine dioxide. The molarity of sulfuric acid was determined by titrating against standard sodium hydroxide using pH meter before each experiment prior to addition of the salts. The samples from the absorber were quantitatively analyzed iodometrically [12] against standard NTS solutions. The chlorine dioxide and chlorine concentrations were determined and calculated on the basis of titration results at neutral ($\text{pH} = 7$) and acidic ($\text{pH} < 2$) conditions. The sodium chloride (Aldrich, USA) consumed in the reactor was quantitatively determined argentometrically [13] against standard silver nitrate solution while chlorate concentrations were obtained iodometrically [14] against standard NTS solutions. The precision of these methods was found better than 2%. The solutions of NTS (Shinyo Pure Chemicals, Japan) and silver nitrate (Kojima, Japan) were prepared and standardized according to the standard procedures.

3. Results and discussion

The reaction of sodium chlorate and sodium chloride in presence of aqueous sulfuric acid was studied at various temperatures and concentrations. The concentrations of chlorine and chlorine dioxide absorbed in absorber and consumption of chloride and chlorate in the reactor were determined by

either iodometric or argentometric titrations at different time intervals and a summary of the kinetic data is reported in Table 1. The stoichiometry [15–19] of the reaction is:



The rate equation of the above reaction can be represented as follows:

$$\frac{dx}{dt} = k \times [\text{NaClO}_3]^\alpha \times [\text{NaCl}]^\beta \times [\text{H}_2\text{SO}_4]^\gamma \quad (6)$$

where k is the rate constant, $[\text{NaClO}_3]$, $[\text{NaCl}]$ and $[\text{H}_2\text{SO}_4]$ are the molar concentrations and α , β and γ are the reaction orders of sodium chlorate, sodium chloride and sulfuric acid, respectively.

3.1. Concentration dependence

The concentration dependence for sodium chlorate or sodium chloride was initially determined at constant temperature with large excess of sodium chloride or sodium chlorate in aqueous sulfuric acid respectively. Thereafter, the concentration dependence of sulfuric acid was determined at constant temperature but with different molar concentrations of acid.

The integration method was applied to determine the order of reaction with respect to sodium chlorate. Different orders were tried. It was found that graph plotted between $\{\log(C_0/C_t)\}$ and time gave a straight line proving the first order. Different sets of experiments were carried out at fixed temperatures, excess of sodium chloride (120.0–150.6 mmol/L) and sulfuric acid (4.254–4.9165 M) by varying the chlorate concentration from 6.108–7.684 mmol/l. Consumption of sodium chloride was less than 4% of the initial charge so

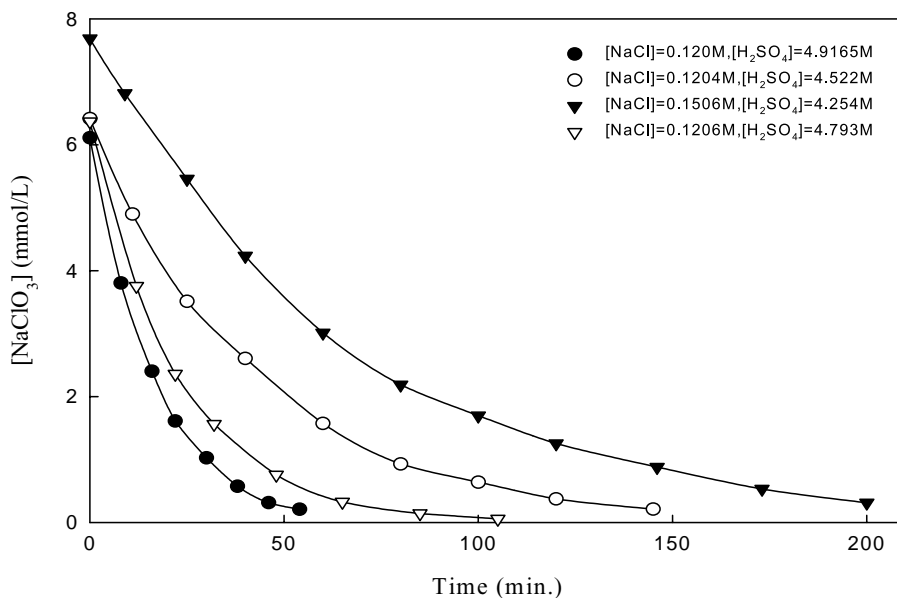


Fig. 2. Decrease in sodium chlorate concentration with time at 308 K.

based ClO₂ generation process. Such a high order has raised doubt whether stoichiometric sulfuric acid concentration is the most appropriate variable to use in determining the rate equation. Empirical acidity scales are commonly used to characterize acidity of solutions of higher concentration where pH scale does not apply.

It has been observed [21–24] that sodium ions increase the acidity, sulfate ions decrease the acidity and chlorate ions have little or no influence on the solution acidity. The acidity functions are often tabulated in logarithm form where H_- equals $(-\log h_-)$. The tables of acidity functions versus stoichiometric concentration of sulfuric acid can be found

elsewhere [24]. H_- acidity scale has been reported earlier by Cox and McTigue [25] and it has been modified for sulfuric acid–sodium sulfate solutions by Indu et al. [26] as follows:

$$-H_- = \log h_- = -2.32 + 2.64a + 0.219b - 1.16(a)^2 - 0.016(b)^2 + 0.44ab \quad (11)$$

where (a) and (b) describe relative and absolute stoichiometric amounts of sulfuric acid and sodium sulfate in solution.

$$a = [\text{H}_2\text{SO}_4]/([\text{H}_2\text{SO}_4] + [\text{Na}_2\text{SO}_4]) \text{ and}$$

$$b = [\text{H}_2\text{SO}_4] + [\text{Na}_2\text{SO}_4]$$

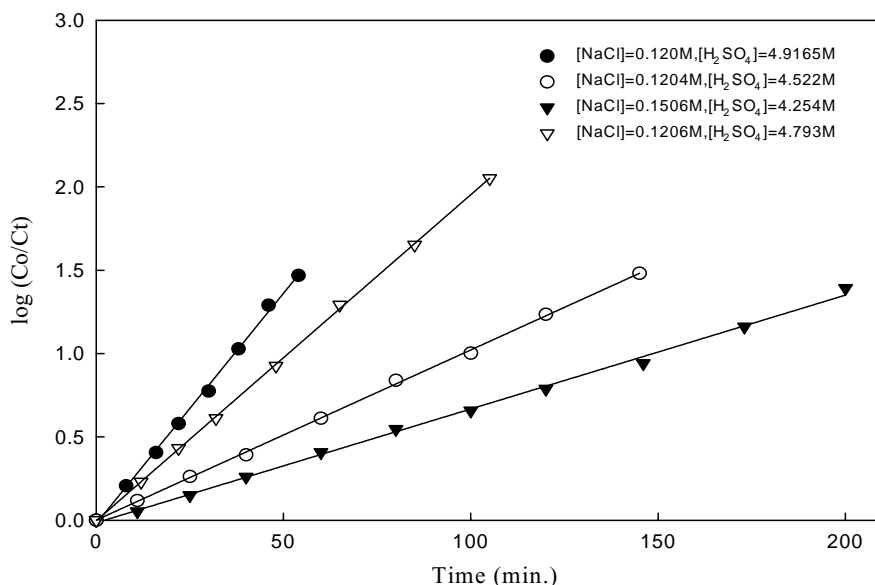


Fig. 3. First order dependence of sodium chlorate concentration at 308 K.

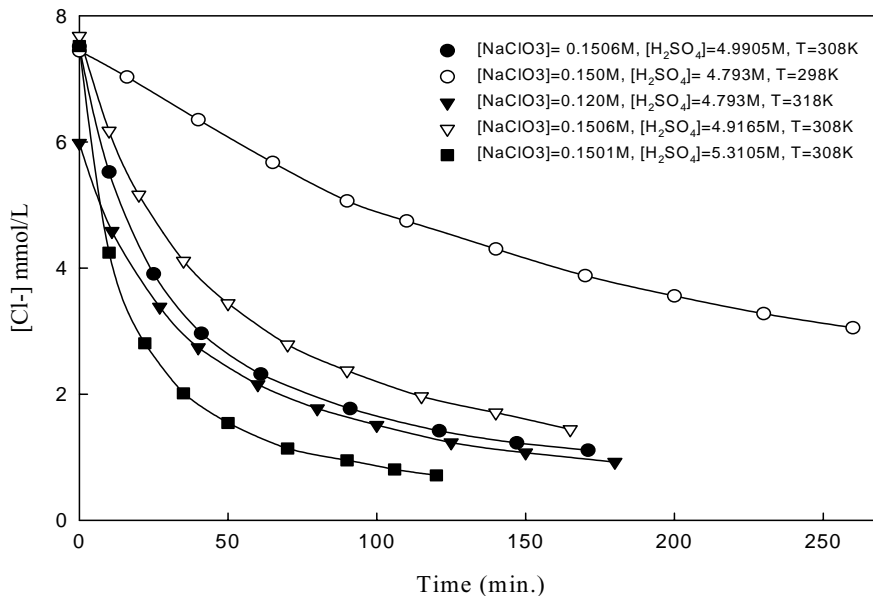


Fig. 4. Decrease in sodium chloride concentration with time.

For aqueous sulfuric acid solutions (in absence of added sodium sulfate), (*a*) equals one and (*b*) equals $[H_2SO_4]$, so Eq. (11) reduces to the following form:

$$-H_- = \log(h_-) = 0.659[H_2SO_4] - 0.016[H_2SO_4]^2 - 0.84 \tag{12}$$

When sodium chlorate or sodium chloride are added in aqueous sulfuric acid solution, Eq. (12) yields very low acidity and it must be corrected for the influence of sodium ions contributed by the sodium chlorate or sodium chloride. Indu et al. [26] suggested addition of quantity $0.12[NaClO_3]$ to the value of ($-H_-$) determined by Eq. (12). Table 2 shows

the value of the parameters *a*, *b* and acidity function ($-H_-$) for all the reaction solutions used in the present study.

To improve the kinetic rate equation, we substituted the acidity function, h_- , in place of $[H_2SO_4]$ to represent the acidity of the solution. The modified rate equation can be written as:

$$\frac{dx}{dt} = A \times \exp\left(\frac{-E_a}{RT}\right) \times [NaClO_3] \times [NaCl]^2 \times (h_-)^\gamma \tag{13}$$

This alternative approach using acidity function in place of molar concentration of sulfuric acid yielded an order of 2.4

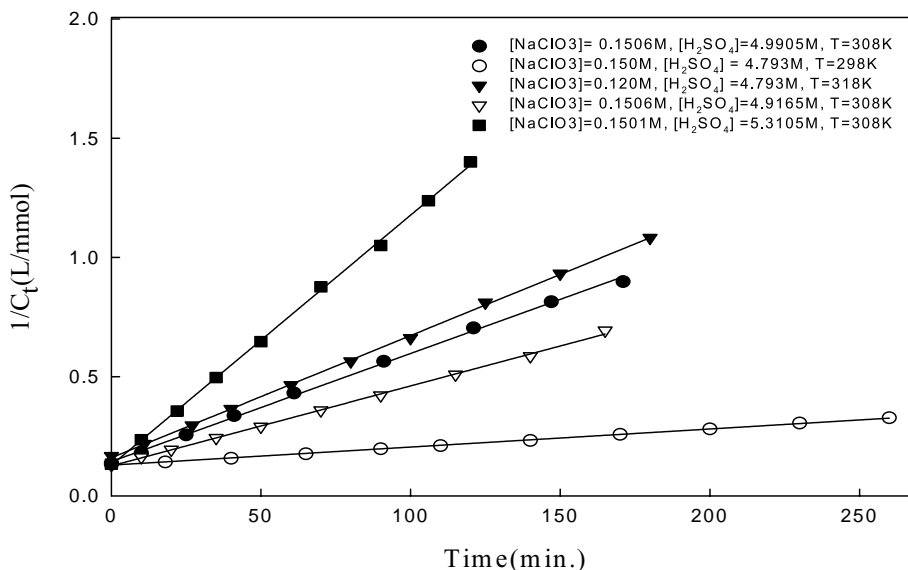


Fig. 5. Second order dependence of sodium chloride concentration.

Table 2
Summary of the data showing acidity functions for various reaction solutions

Temperature (K)	[NaClO ₃] molar	[NaCl] molar	[H ₂ SO ₄] molar	<i>a</i>	<i>b</i>	<i>H</i> ₋ (uncorrected)	<i>H</i> ₋ (corrected)
308	0.1506	0.0075	4.9905	1	4.9905	2.0503	2.0692
298	0.1500	0.0074	4.7930	1	4.7930	1.9510	1.9699
318	0.1200	0.0060	4.7930	1	4.7930	1.9510	1.9661
308	0.1506	0.0077	4.9165	1	4.9165	2.0132	2.0322
308	0.1501	0.0075	5.3105	1	5.3105	2.2084	2.2273
308	0.0061	0.1200	4.9165	1	4.9165	2.0132	2.0284
308	0.0064	0.1204	4.5220	1	4.5220	1.8128	1.8280
308	0.0077	0.1506	4.2540	1	4.2540	1.6738	1.6928
308	0.0064	0.1206	4.7930	1	4.7930	1.9510	1.9663
308	0.1504	0.0075	4.778	1	4.7780	1.9434	1.9624

with respect to sulfuric acid. Furthermore, this reaction order remained unaffected of chlorate/chloride ratio. The graph between $\log \{C/[NaCl]^2\}$ or $\log \{S/2[NaClO_3]\}$ and $-H_-$ are shown in Figs. 6 and 7.

3.2. Temperature dependence

Reaction kinetics was studied by performing experiments at different temperatures i.e. 25, 35 and 45 °C. The rate constants at different temperatures were obtained from the slopes of the straight lines in Fig. 5 at various molar concentrations of chlorate, chloride and sulfuric acid. The Arrhenius plot of the rate constants is plotted in Fig. 8. The values of activation energy ($E_a = 81.84$ kJ/mol) and pre-exponential Arrhenius parameter ($A = 2.403 \times 10^2$) are determined from the slope and intercept of Fig. 8, respectively.

Using molar concentration of sulfuric acid, the developed rate equation that best fits the experimental data is:

$$\frac{dx}{dt} = 2.403 \times 10^2 \times \exp\left(\frac{-9843.2}{T}\right) \times [NaClO_3] \times [NaCl]^2 \times [H_2SO_4]^{14.2} \quad (14)$$

However, when $[H_2SO_4]$ is replaced by acidity function, h_- , the improved rate equation for chloride based chlorine dioxide generation process can be expressed as:

$$\frac{dx}{dt} = 2.639 \times 10^7 \times \exp\left(\frac{-9944.6}{T}\right) \times [NaClO_3] \times [NaCl]^2 \times (h_-)^{2.4} \quad (15)$$

where the values of activation energy ($E_a = 82.68$ kJ/mol) and pre-exponential Arrhenius parameter ($A = 2.639 \times 10^7$) are determined from the slope and intercept of Arrhenius plot in Fig. 8. Eqs. (14) and (15) are valid for high chlorate/chloride ratio, at which reaction follows the stoichiometry of Eq. (5). The comparison of experimental and calculated data for all the runs used in the rate. Eq. (14)

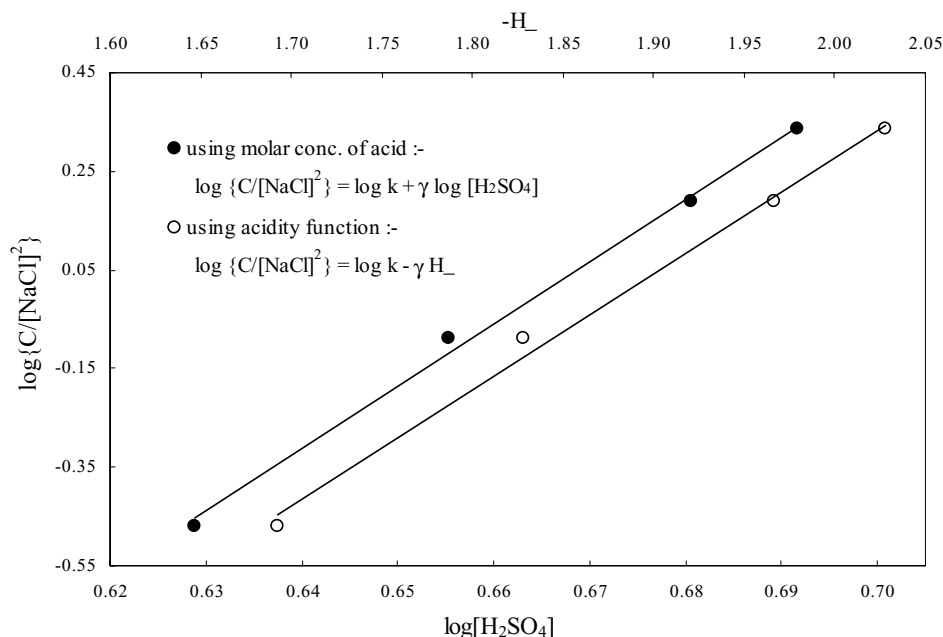


Fig. 6. Determination of the reaction order (γ) with respect to sulfuric acid at low chlorate/chloride ratio.

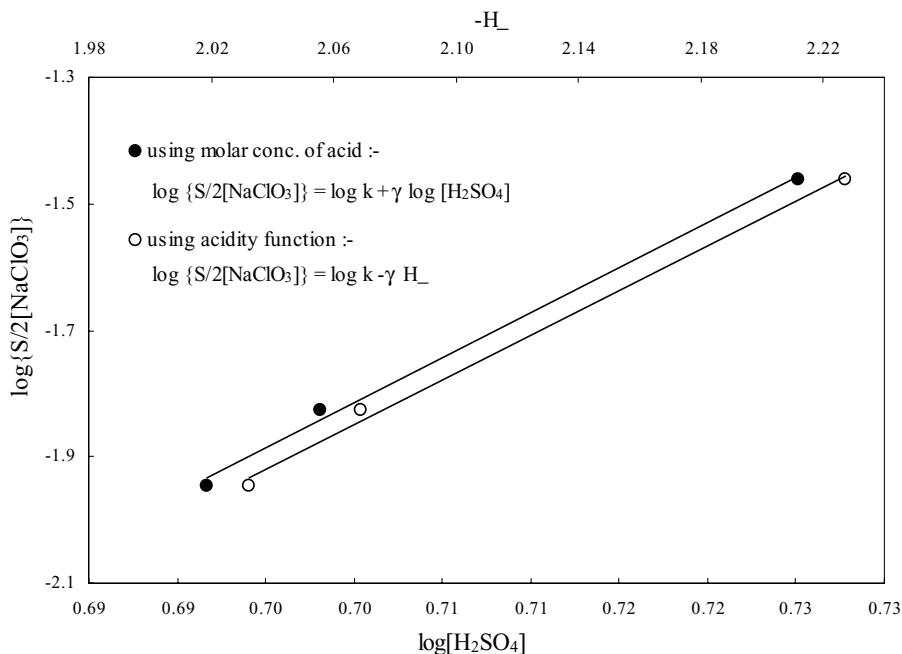


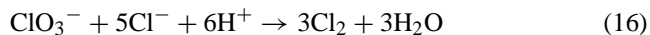
Fig. 7. Determination of the reaction order (γ) with respect to sulfuric acid at high chlorate/chloride ratio.

and (15) are shown in Figs. 9 and 10, respectively. Both equations presented good agreement of the experimental and calculated data at high chlorate/chloride ratio.

3.3. Reaction mechanism

It is also observed that chlorine dioxide to chlorine ratio is markedly affected by chlorate/chloride ratio. If the chlorate/chloride ratio is equal to or higher than one, then stoichiometry of the reaction corresponds to Eq. (5) and ratio of chlorine dioxide to chlorine gas is nearly two. However, if chlorate/chloride ratio is less than one, then the produc-

tion of chlorine is enhanced and ClO_2/Cl_2 ratio decreases to about 0.5–0.6 due to occurrence of the following side reaction [18,19,27]:



In the light of above discussion, the overall mechanism of the chloride–chlorate reaction in aqueous sulfuric acid seems to have the following steps:

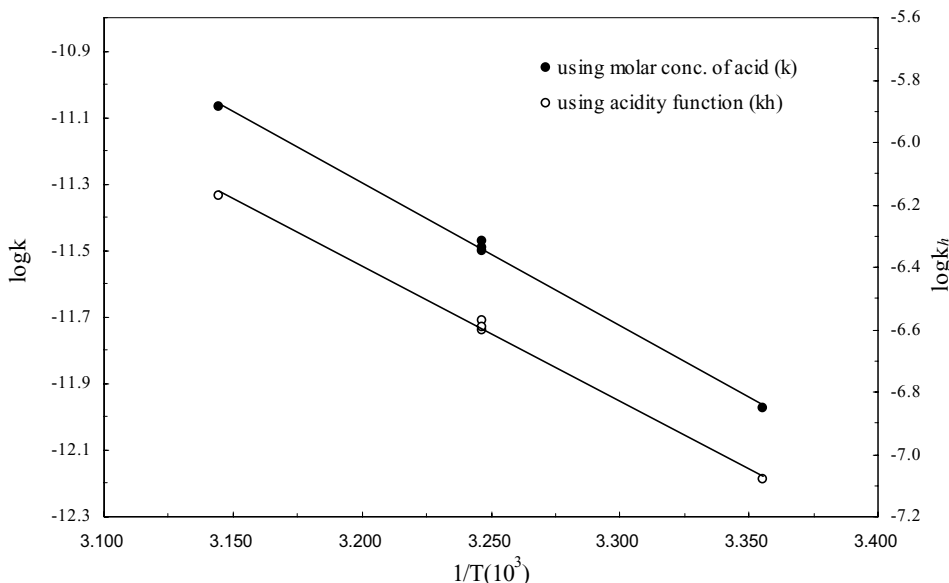
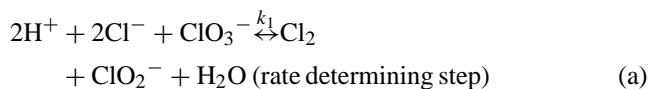


Fig. 8. Arrhenius plots of the rate constant.

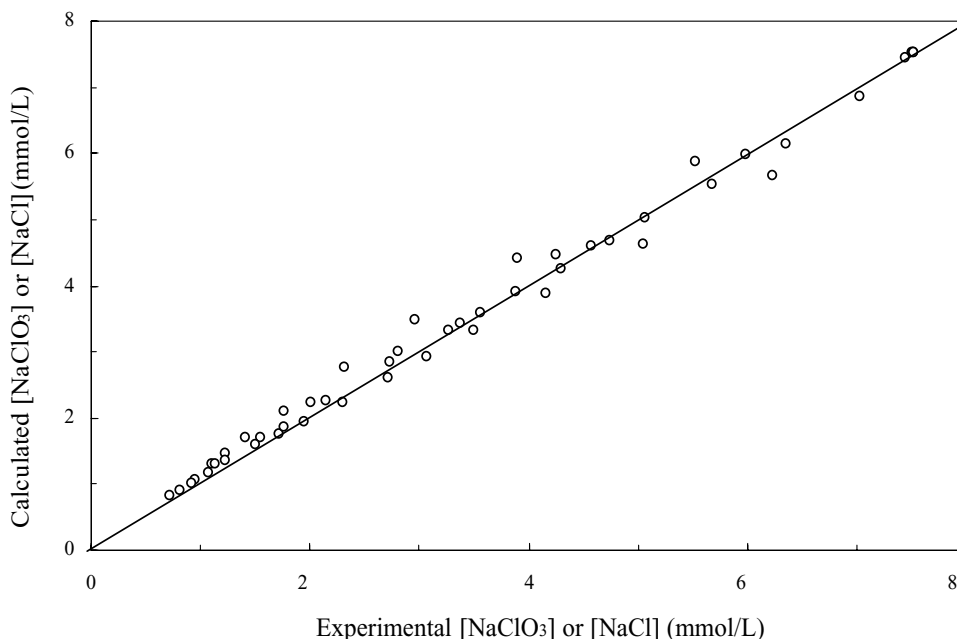
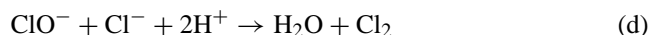


Fig. 9. Comparison of experimental concentrations of chlorate or chloride and concentrations calculated using rate law of Eq. (14).



The main stoichiometry of the reaction is described by the combination of first two steps i.e. (a) and (b), where step ‘a’ is rate controlling reversible step. However, the enhanced production of chlorine is attributed due to contribution of last two steps i.e. c and d. Eq. (16) is obtained by combining step a, c and d.

At high chlorate concentration when reaction follows the stoichiometry of Eq. (5), the rate of formation of chlorine-dioxide from step (b) can be written as:

$$\frac{d[\text{ClO}_2]}{dt} = 2k_2[\text{H}^+]^2[\text{ClO}_3^-][\text{ClO}_2^-] \quad (17)$$

Applying steady state approximation, chlorite concentration can be expressed as:

$$[\text{ClO}_2^-] = \frac{k_1[\text{H}^+]^2[\text{Cl}^-]^2[\text{ClO}_3^-]}{k_{-1}[\text{Cl}_2] + k_2[\text{H}^+]^2[\text{ClO}_3^-]} \quad (18)$$

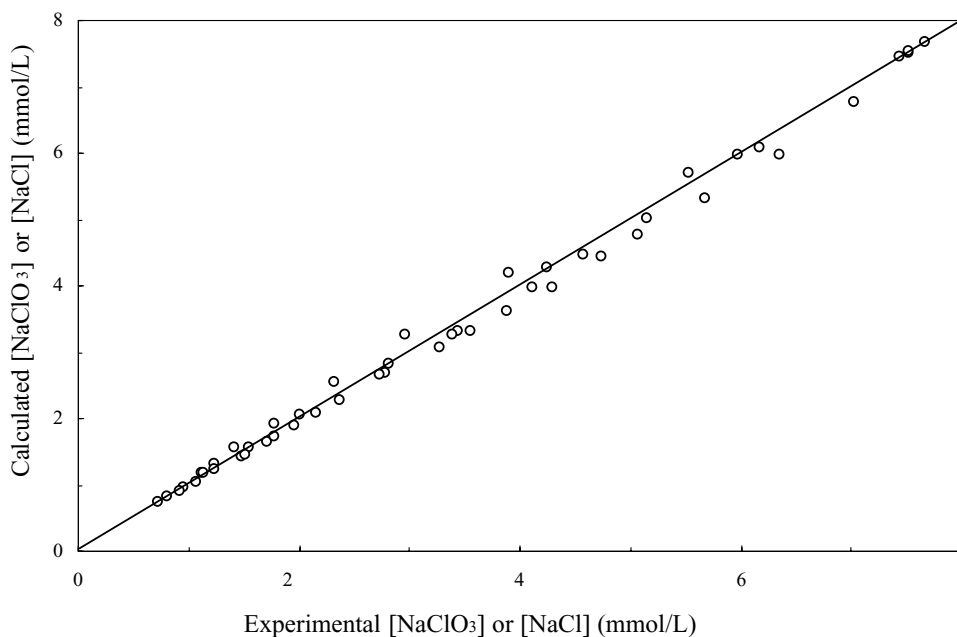


Fig. 10. Comparison of experimental concentrations of chlorate or chloride and concentrations calculated using rate law of Eq. (15).

Putting chlorite concentration in Eq. (17), we get:

$$\frac{d[\text{ClO}_2]}{dt} = \frac{2k_1k_2[\text{H}^+]^4[\text{Cl}^-]^2[\text{ClO}_3^-]^2}{k_{-1}[\text{Cl}_2] + k_2[\text{H}^+]^2[\text{ClO}_3^-]} \quad (19)$$

At higher chlorate concentration, first term in the denominator can be neglected, so it can be written as:

$$\frac{dx}{dt} = \frac{1}{2} \frac{d[\text{ClO}_2]}{dt} = k_1[\text{H}^+]^2[\text{Cl}^-]^2[\text{ClO}_3^-] \quad (20)$$

4. Conclusion

The reaction of sodium chlorate and sodium chloride was found to be first order with respect to sodium chlorate, second order with respect to sodium chloride and very high dependence on molar concentration of acid of the order of about 13–14 respectively. The reaction rate is highly sensitive to acid concentration. Alternative approach using acidity function in place of molar concentration of acid yielded an order of 2.4 with respect to sulfuric acid. The chlorine dioxide to chlorine ratio is affected by chlorate to chloride ratio. Enhanced production of chlorine is due to a side reaction, which is favored by higher chloride concentrations. Hence it is advisable to take higher concentrations of chlorate and sulfuric acid in the reactor and then injecting continuously the concentrated solution of chloride slowly into the reactor. It will not only reduce the production of chlorine but also help in the controlled production of chlorine dioxide. The proposed reaction mechanism is well supported by the experimental observations. The improved rate equation gives good agreement between experimental and calculated data and describes the consumption of chlorate and chloride as well as production of chlorine dioxide and chlorine very well during the course of the reaction.

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