Kinetics of the Preparation of Chlorine Dioxide by Sodium Chlorite and Hydrochloric Acid at Low Concentration

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The kinetics of the reaction between sodium chlorite and hydrochloric acid is studied at various temperatures and molar concentrations of chlorite and acid at low concentrations. The reaction rate law is established, and macrokinetics formula is obtained. Reaction has been found 1 and 1.39 order with respect to chlorite and hydrochloric acid respectively when preparing chloride dioxide using low concentrations of sodium chlorite and hydrochloric acid. The temperature dependence of the reaction is also investigated and pre-exponential Arrhenius parameter as well as activation energy are determined.

1. Introduction

Chloride dioxide (ClO_2) is usually used as an oxidant for pulp bleaching and disinfection. For its application in water treatment, chloride dioxide can achieve a good disinfection effect without producing chlorinated organic matters such as trihalomethanes (THMs) and chlorophenol that are carcinogens or mutagens, which was reported by Yu and Zhang (2012).

Under normal temperature, chloride dioxide exists as a gas that has an excellent antibacterial and disinfection effect on a variety of microorganisms. Moreover, chloride dioxide does not produce toxic chlorides and possesses a better diffusibility, penetrability and use uniformity compared with liquid chlorine dioxide. These features make chloride dioxide particularly suitable for the prevention and treatment of microbial pollution within a large space. Disinfection with gaseous chlorine dioxide has an antibacterial effect that is 400-2000 times stronger than that of other similar air disinfection and purification techniques. Producing no harmful impact on humans, chlorine dioxide is classified as a disinfectant of A1 safety class by the World Health Organization. Zhang (2012) reported the technology development and application of Chlorine dioxide disinfection. Xi (2012) studied the disinfection effect using chlorine dioxide in public space.

Chlorine dioxide is generally prepared using sodium chlorite or sodium chlorate by reduction reaction in acidic conditions. When sodium chlorate is used as the raw material, sulfur dioxide, methanol or hydrogen peroxide is usually chosen as the reductant to produce chlorine dioxide under acidic conditions. But this reaction produces many undesired byproducts, typically chlorine.

In recent years, the generating method and kinetics of chlorine dioxide has often been studied. Wang (2008) and Yang (2007) studied the production methods of chlorine dioxide; Chen (2003), Qian (2004), Shi (1999) and Zhu (2011) studied the kinetics of the chlorine dioxide from hydrogen peroxide. Liu (2009) studied the kinetics of chlorine dioxide preparation by R5 method in conventional heating and microwave heating. Jin (2008) studied the kinetic of formation of high- purity chlorine dioxide gas using sodium chlorate as raw materials. Li (2013) studied the kinetics of the reaction for generation of chlorine dioxide from sodium chlorate and hydrochloric acid, and conclude that the rate equation of the reaction system was a formula with mixed-order (combination of first-order and second-order) towards ClO_3^-.

B.R.Deshwal (2004) studied the reaction between sodium chlorate and sodium chloride in presence of aqueous sulfuric acid and the rate law is established. The temperature dependence of the reaction is also investigated and pre-exponential Arrhenius parameter as well as activation energy are determined. Fang (2013) reported the preparation of chlorine dioxide by sodium chlorite as raw material. His main research is

the reaction between sodium chlorite and slow release activator (such as sodium persulfate and potassium peroxymonosulfate) to prepare solid controlled-release chlorine dioxide.

High-purity chlorine dioxide gas can be prepared by the reaction of sodiumchlorite and hydrochloric acid for ambient air disinfection. The stoichiometric equation is expressed as follows:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 \uparrow + 5NaCl + 2H_2O \tag{1}$$

Since chlorine dioxide gas is explosive and tends to decompose upon heating, it is not suitable for storage and transport, hence it is usually produced immediately before use. For disinfection of ambient air in a large confined space, the concentration of chlorine dioxide needs to be maintained at 0.1-0.28 mg/m^3. An excess concentration is harmful to humans, while a low concentration has poor disinfection effect.

In order to control the concentration of chlorine dioxide in the ambient air, the reaction needs to be tightly controlled at a low rate. Moreover, the reaction rate needs to be adjusted timely based on the concentration of chlorine dioxide in the air. One effective method to accurately calculate the addition amount of reactants and to reduce the reaction rate is to reduce the concentration of reactants. Research on generating chlorine dioxide with low concentrations of sodium chlorite and hydrochloric acid to generate chlorine dioxide has not been reported. In this study, sodiumchlorite and hydrochloric acid were used to produce chlorine dioxide, and the kinetic characteristics of the reaction at low concentrations were discussed. A macroscopic reaction rate equation was built with the purpose of providing guidance for the design of the reactor and for further applications of the new preparation technique.
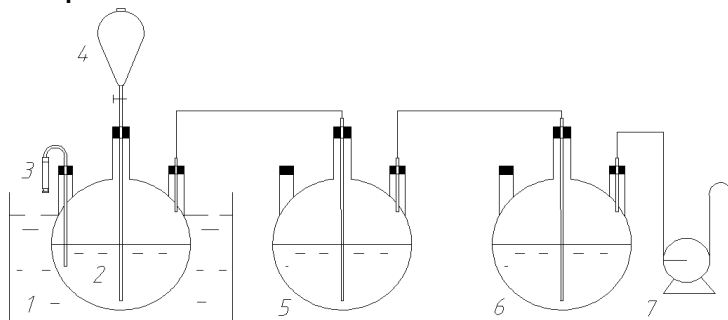
2. Experiment

2.1 Experiment reagents
Sodium chlorite (A.R), hydrochloric acid (A.R 37.5%), potassium iodide (A.R), sodiumthiosulphate (A.R).

2.2 Equipment
Thermostatic water bath, vacuum pump.

2.3 Experimental facilities

1. Thermostatic water bath 2. Reactor 3. Sample injector 4. Feeding funnel and air inlet 5. Absorption bottle for potassium iodide 6. Absorption bottle for potassium iodide 7. Vacuum pump

Figure 1: Experimental facilities

2.4 Experimental procedure
Thermostatic water bath was adjusted to a certain temperature, and dilute solution of sodiumchlorite was added into the reaction flask. Meanwhile, hydrochloric acid solution was added into the separating funnel. The vacuum pump was started. After pressure adjustment, the separating funnel was opened, and the hydrochloric acid solution was added all in once to initiate the reaction. Time zero started from this moment.

For every 2-3 min, the reaction liquid was sampled with a 1 ml syring. The concentration of chlorite in the sample was determined by five-stepiodometry, and the conversion rate of sodium chlorite was calculated at each sampling.

The generated chlorine dioxide gas was discharged under negative pressure after passing through potassium iodide solution repeatedly. After the reaction was completed, the thermostatic water bath stopped, the pressure was adjusted to atmospheric pressure, and the vacuum pump was turned off.

2.5 Measurements and analysis
The concentration of chlorite was determined by five-step iodometry, and the concentration of hydrogen ions was calculated by subtraction.

3. Results and discussion

According to the equation of reaction of sodium chlorite and hydrochloric acid (1), if the reaction rate was measured by the amount of sodium chlorite consumed, the reaction kinetic equation can be expressed as follows:

$$-\frac{d[NaClO_2]}{dt} = k[NaClO_2]^{\alpha}[HCl]^{\beta} \tag{2}$$

Where $[NaClO_2]$ and $[HCl]$ are the molar concentrations of sodium chlorite and hydrochloric acid, respectively; α and β are the order of reaction with respect to sodium chlorite and hydrochloric acid, respectively. The reaction conditions, namely, temperature and reactant concentration, were changed, and the reaction liquid was sampled at different time points. By measuring the changes of the concentration of sodium chlorite with time, the order of reaction with respect to the reactant and the reaction rate constants were fitted. On this basis, the reaction kinetic equation was derived.

First, the temperature was fixed at 298.15 K and the initial mass concentration of sodium chlorite was at approximately 0.2%. The addition amount of hydrochloric acid was changed, and the variation of the concentration of sodium chlorite was recorded under each addition amount. We got 7 groups of experimental data numbered as group 1 to group 7.

Then the initial mass concentration of sodium chlorite was fixed at approximately 0.2% and that of hydrochloric acid at 0.32mol/L. The temperature was changed, and the variation of the concentration of sodium chlorite over time was observed. 7 groups of experimental data were got and numbered as group 8 to group 14.

3.1 Determination of the order of reaction

Because sodium chlorite is expensive, excess amount of hydrochloric acid is usually added in real production. This was also the strategy used in the present study. Because the concentration of hydrochloric acid was far excessive, it changed very little during reaction, so the concentration of hydrochloric acid [HCl] can be considered as a constant. Trial calculation and fitting were performed under different preset order of reaction with respect to sodium chlorite. It was found that the $\ln(C_0/C_t)$ of sodium chlorite (where C_0 and C_t were the molar concentrations of sodium chlorite at time 0 and t, respectively) was a linear relationship with time. Thusthe order of reaction α with respect to sodium chlorite was 1, as shown in Fig. 2 and Fig. 3.
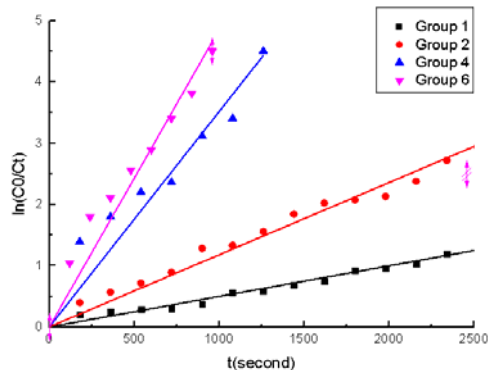

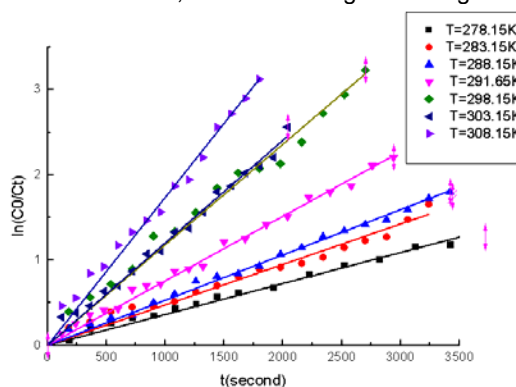*Figure 2: Relationship between $\ln(C_0/C_t)$ of sodiumchlorite and time t at 298.15K*

Figure 3: Relationship between $\ln(C_0/C_t)$ of sodiumchlorite and time t at different temperature

Then the reaction rate equation (2) is changed into

$$-\frac{d[NaClO_2]}{dt} = k[NaClO_2] \ [HCl]^{\beta} \tag{3}$$

After sorting, equation (3) becomes

$$-\frac{d[NaClO_2]}{[NaClO_2]} = k[HCl]^{\beta} dt \tag{4}$$

When the temperature is fixed, the reaction rate constant k is a constant.With a great excess of hydrochloric acid,thus [HCl] can be approximated as a constant. Integration is performed for both sides of equation (4)to derive

$\ln(C_0/C_t)=k[HCl]^{\beta} t$

where C_0 and C_t are the molar concentrations of sodium chlorite at time 0 and t, respectively. Therefore, the slopes of each line in Fig. 2 and Fig. 3 are calculated as follows:
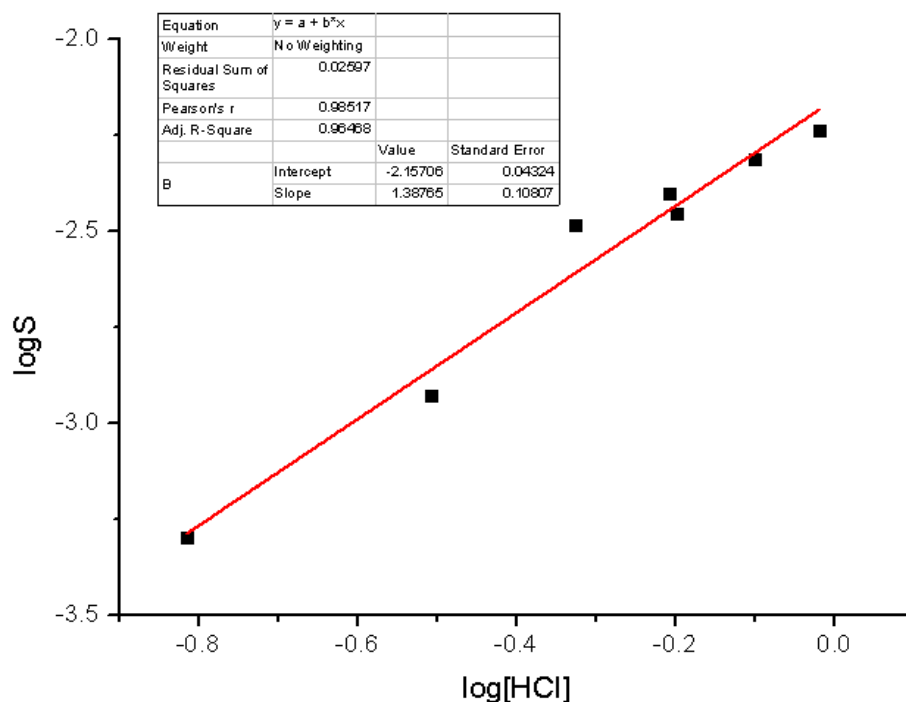
$S=k[HCl]^\beta$

Logarithm is taken on the two sides:

$logS=logk+\beta log[HCl]$

When the temperature is fixed on 298.15K, the reaction rate constant k is the same. The slope S of each line fitted using the data group 1 to group 7 and the average concentration of hydrochloric acid before and afterreaction were calculated. The table 1 below was obtained.

Table 1: Slopes of lines fitted using each group of data and the corresponding concentrations of hydrochloric acid at 298.15K

	Group1	Group2	Group3	Group 4	Group 5	Group 6	Group 7
Slope S	0.000503	0.001180	0.003288	0.003518	0.003950	0.004857	0.005798
[HCl](mol/L)	0.1532	0.3113	0.4720	0.6324	0.6194	0.7938	0.9556
log[HCl]	-0.8147	-0.5068	-0.3261	-0.1990	-0.2080	-0.1003	-0.0197
logS	-3.2984	-2.9282	-2.4830	-2.4537	-2.4034	-2.3137	-2.2367

Straight lines were plotted with log[HCl] on the x axis and logS on the y axis (Table 1). The slope of the line was the reaction order β with respect to hydrochloric acid, which was 1.39 (Fig. 4).

Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	0.02597	
Pearson's r	0.98517	
Adj. R-Square	0.96468	
	Value	Standard Error
B Intercept	-2.15706	0.04324
Slope	1.38765	0.10807

Figure 4: Calculation of the reaction order β with respect to hydrochloric acid

With the order of reaction obtained, the reaction rate equation changes into

$$-\frac{d[NaClO_2]}{dt}=k[NaClO_2]\ [HCl]^{1.39}$$

(5)

3.2 Calculation of activation energy and pre-exponential factor
In formula (5), k is rate constant of the reaction expressed as

$$k = A \times e^{-\frac{Ea}{RT}}$$

where A is pre-exponential factor, and Ea is the activation energy.

According to formula (4), $k = \dfrac{S}{[HCl]^{\beta}}$, thus $k = A \times e^{-\frac{Ea}{RT}} = \dfrac{S}{[HCl]^{\beta}}$.

Taking logarithm on the two sides, there is

$\ln k = lnA - \dfrac{Ea}{RT} = \ln S - \beta \ln[HCl]$. That is $\ln S - \beta \ln[HCl] = lnA - \dfrac{Ea}{RT}$.

In order to derive the equation of rate constant k, the slope S of each line under different temperatures (Fig. 3) was calculated. The average concentration of hydrochloric acid [HCl] in the reaction liquid under different temperature was also calculated and shown in Table 2. The values of $\ln S - \beta \ln[HCl]$ and -1/T were further calculated under each temperature.

Table 2: Relationship between $\ln S - \beta \ln[HCl]$ and -1/T under different temperature

	Group8	Group9	Group10	Group11	Group12	Group13	Group14
T(K)	278.15	283.15	288.15	291. 65	298.15	303.15	308.15
Slope S	0.0003631	0.0004748	0.0005308	0.0007571	0.00118	0.0012	0.00174
[HCl]	0.3158	0.3144	0.3137	0.3133	0.3113	0.3121	0.3106
βln[HCl]	-1.6022	-1.6084	-1.6115	-1.6132	-1.6221	-1.6186	-1.6253
lnS-βln[HCl]	-6.3187	-6.0443	-5.9297	-5.5728	-5.1201	-5.1069	-4.7286
-1/T	-0.003595	-0.003532	-0.003470	-0.003429	-0.003354	-0.003299	-0.003245

Fig. 5 was plotted according to the above data.

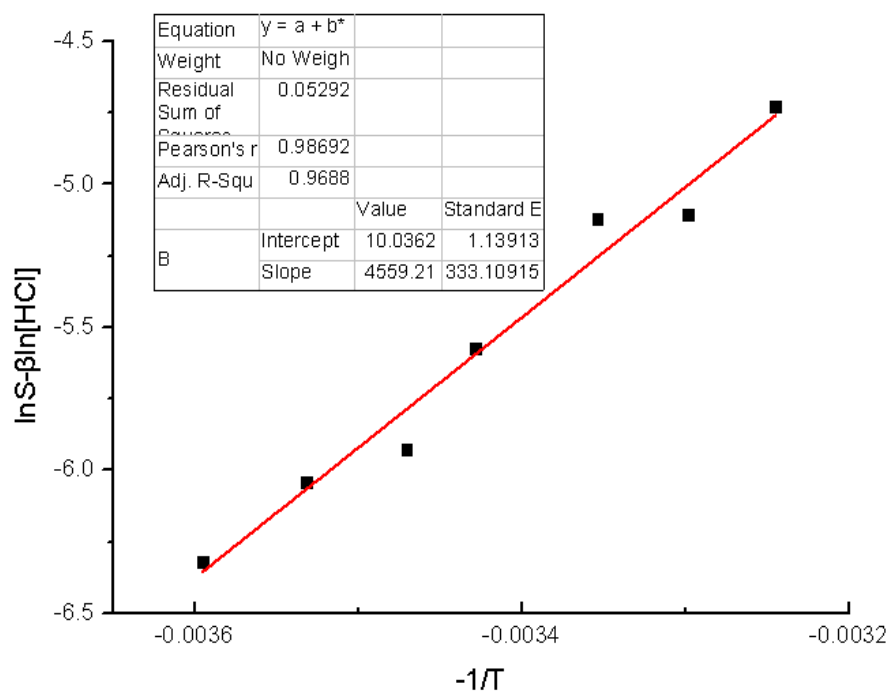| Equation	y = a + b*		
Weight	No Weigh		
Residual Sum of Squares	0.05292		
Pearson's r	0.98692		
Adj. R-Squ	0.9688		
		Value	Standard E
B	Intercept	10.0362	1.13913
	Slope	4559.21	333.10915

Figure 5: Gain of activation energy and pre-exponential factor

According to Figure 5, the slope
S=Ea/R=4559.2
then Ea=8.314×4559.2=37905 J/mol;
The intercept lnA=10.036,
then the pre-exponential factor A=2.283×10⁴.
So the constant of reaction rate

54

$$k = 2.283 \times 10^4 \times e^{-\frac{37905}{RT}}.$$

4. Conclusions

To conclude, the macroscopic rate equation for the reaction between sodium chlorite and hydrochloric acid was fitted as

$$-\frac{d[NaClO_2]}{dt} = 2.283 \times 10^4 \times e^{-\frac{37905}{RT}} \times [NaClO_2] \times [HCl]^{1.39}$$

This equation lays the theoretical basis for reactor design and further development and application of the new technique.

Acknowledgments

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