Study on ClO_2 Production from $NaClO_3$ to Remove SO_x and NO_x

Bal Raj Deshwal , Dong-Seop Jin[1], Hag-Dong Kim[1], Hang-Dae Jo[1], Won-Kil Choi[1] , Hyung-Keun Lee*[1]

Department of Chemistry, A.I.J.H.M. College, Rohtak (Haryana) INDIA

Korea Institute of Energy Research (KIER), Daejeon.[1]

(hklee@kier.re.kr*)

Abstract

Reaction kinetics of ClO_2 production from sodium chlorate is studied in a well-stirred reactor at various temperatures and molar concentrations by analyzing the consumption of chlorate and chloride or production of ClO_2 and Cl_2 using iodometric or argentometric titrations. The kinetic rate equation is established. The experimental ClO_2/Cl_2 ratio is found higher than the theoretical one as expected by main stoichiometry of the reaction. Effect of $NaClO_3/NaCl$ ratio, temperature and acid strength on ClO_2/Cl_2 ratio is investigated. Reaction mechanism and possible side reactions responsible for the variation in ClO_2/Cl_2 ratio are proposed.

1. Introduction

There is a growing concern to develop simpler, easier to operate, more efficient and economical technique for the chlorine dioxide generation. Chlorine dioxide has achieved remarkable commercial attention not only due to environmental concern but also due to its wide applications in the fields of bleaching, oxidation and disinfection. It is always generated on-site because of its unstable nature and risk of rapid decomposition. Most of small and medium scale generators use sodium chlorite as the precursor material particularly for water treatment and disinfection applications as they require high purity (i.e. Cl_2 free) waters. Others applications, which need large quantities of chlorine dioxide utilize sodium chlorate as the raw material. The economic considerations for the ClO_2 generation play 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 [Woodside and Macleod, 1953], methanol [Ni and Wang, 1997], sodium chloride [Rapson,1966], hydrochloric acid or hydrogen peroxide [Burke et al., 1993] etc. The choice of reducing agent has been influenced by operating conditions, reaction byproducts and economics of the process. Until recently, most of chlorine dioxide was produced by reducing sodium chlorate with help of sodium chloride. The proposed stoichiometry of chloride-chlorate reaction is as follows:

$$2NaClO_3 + 2NaCl + 2H_2SO_4 \rightarrow 2ClO_2 + Cl_2 + 2Na_2SO_4 + 2H_2O \quad (1)$$

Theoretically, it gives euchlorine; a mixture of chlorine dioxide and chlorine in molar ratio of two. This process gives highest yield of ClO_2 at the lowest cost among all commercial processes. The present work is aimed to investigate the reaction kinetics and to enhance ClO_2/Cl_2 ratio.

2. Material and Methods

The experimental system is composed of a reactor and an absorber. Reactor is well-stirred sealed vessel. Continuous stirring is provided by a mechanical agitator. Temperature is controlled by water thermostat within ± 0.1°C. Nitrogen gas was purged through the reaction mixture using a bubbling device at a flow rate of 2L/min. Reaction mixture involved sodium chlorate, sodium chloride and sulfuric acid. The absorber consisted of ca. 2% carbonate buffered potassium iodide solution. Samples from reactor were quantitatively analyzed for chloride [Tang and Gordon, 1980] and chlorate [Vogel, 1989] and that of absorber were analyzed for Cl_2 and ClO_2 [Aieta at al.] using auto-titrator

(Metrohm-Swiss). The potentiometric titration system included a 670 titroprocessor, 730 sample changer, 665 dosimat and platinum electrode. 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.

3. Results and Discussion

Chloride-chlorate reaction as shown in equation-1 is the basis of R-2 process for chlorine dioxide generation. This process is extremely simple to operate and highly cost effective. Kinetics of this reaction was studied at various temperatures and concentrations of chlorate, chloride and sulfuric acid.

3.1 Kinetics: *Concentration Dependence*

The integration method was applied to determine the order of reaction w.r.t sodium chlorate. Different orders were tried. It was found that graph plotted between {log (C_o/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 and sulfuric acid by varying the chlorate conc. The constancy in the value of k proved the first order dependence on sodium chlorate, which is depicted in Figure 1.

The reaction order with respect to sodium chloride was also determined in the same manner. It was found that $\beta = 2$ provide the best fit of the kinetic data. Second order dependence on chloride conc. is represented in Figure 2. The slope (S) of the straight lines in Figure 1 can be written as follows:

$$S = \frac{2k}{2.303} \times [NaCl]^2 \times [H_2SO_4]^{\gamma} \qquad (2)$$

Rearranging the equation 2 and then taking the logarithm, leads to,

$$\log \frac{C}{[NaCl]^2} = \gamma \log [H_2SO_4] + \log k \qquad (3)$$

Here C is {S×2.303/2}. Therefore, by plotting the log {C/ $[NaCl]^2$} versus {log [H_2SO_4]} we obtained a straight line relationship. The results at 35°C and constant chloride conc. are demonstrated in Figure 3. The slope of the straight line (order w.r.t sulfuric acid) was found to be 12.6.

Temperature Dependence

Reaction kinetics was studied by performing experiments at 25, 35 and 45°C. The rate constants at different temperatures were obtained from the slopes of the straight lines in figure 1 and 2. The Arrehenius plot of the rate constants is plotted in Figure 4. The values of activation energy (E_a) and Arrehenius parameter (A) were determined from the slope and intercept respectively.

3.2 Factors Affecting ClO_2/Cl_2 Ratio and Mechanism Involved

The theoretical ClO_2/Cl_2 (η) ratio of chloride-chlorate reaction is equal to 2. Hong and Rapson [1968] found that at low chlorate/chloride ratios, production of Cl_2 is enhanced and η decreases below 2. However, no work ever has been reported to investigate the reaction conditions which may enhance the ClO_2/Cl_2 ratio, henceforth it is the major substance of the present work.

Effect of Chlorate/Chloride Ratio

Chlorate/chloride ratio is the major factor responsible for influencing the ClO_2/Cl_2 ratio. The graph plotted between η and Φ-values is presented in figure 5. When chlorate/chloride ratio was taken in the range of 0.5 to 1, reaction followed the main stoichiometry with no side reaction, yielding ClO_2

and Cl_2 in molar ratio of about 2; however if the Φ-value is decreased below 0.5, then production of Cl_2 is enhanced due to occurrence of following side reaction [Hong and Rapson, 1968]:

$$ClO_3^- + 5Cl^- + 6H^+ \rightarrow 3Cl_2 + 3H_2O \tag{4}$$

When chlorate/chloride ratio was taken higher than one, then ClO_2/Cl_2 ratio exceeded two and touched the maximum of ~3.4 at Φ-value of four. The enhancement in ClO_2/Cl_2 ratio seems to be due to another side reaction between chlorite and chlorine gas as follows:

$$2ClO_2^- + Cl_2 \rightarrow 2Cl^- + 2ClO_2 \tag{5}$$

Chlorite is formed as an intermediate product in the main chloride-chlorate reaction. It is noteworthy here that chlorine-chlorite reaction is a rapid reaction [Emmenegger and Gordon, 1967].

Effect of Molar Concentration of Acid and Temperature

The effect of conc. of sulfuric acid on the ClO_2/Cl_2 ratio was investigated by performing experiments at chlorate/chloride ratio of 0.05 and 1 and temperature of 25 and 35°C varying the molar conc. of sulfuric acid and are presented in figure 6. There was no significant improvement in η-values, though optimum conc. of acid is indirectly influenced by chlorate/chloride ratio.

Experiments were performed at constant chlorate/chloride ratio of 1 and 20 in 4.795M acid at 25, 35 and 45°C, yet there was no appreciable change in ClO_2/Cl_2 ratio as shown in figure 7.

4. Conclusions

In conclusion, η-value is not affected at all by temperature and conc. of acid; however chlorate/chloride ratio has remarkable effect on ClO_2/Cl_2 ratio. The rate equation for chloride based chlorine dioxide generation process can be expressed as:

$$\frac{dx}{dt} = 1.152 \times 10^2 \times \exp(-9838.65/T) \times [NaClO_3] \times [NaCl]^2 \times [H_2SO_4]^{12.6} \tag{6}$$

The comparison of experimental and calculated data for all the runs used in the developed rate equation is shown in Figure 8. It shows the good agreement of the experimental and calculated data.

5. References

Aieta, E.M., Roberts, P.V. and Hernandez, M., "Determination of Chlorine Dioxide, Chlorine, Chlorite and Chlorate in Water Research and Technology", J. Amer. Water Works Assoc., **76,** 64 (1984).

Burke, M., Tenney, J., Indu, B., Hoq, M.F., Carr, S. and Ernst, W.R., "Kinetics of HydrogenPeroxide - Chlorate Reaction in the Formation of Chlorine Dioxide", Ind. Eng. Chem. Res., **32,** 1449 (1993).

Emmenegger, F. and Gordon, G., "The Rapid Interaction between Sodium Chlorite and Dissolved Chlorine", Inorg.Chem., **6**, 633 (1967).

Hong, C.C. and Rapson, W.H., Can. J. Chem. Eng., **46**, 2053 (1968).

Ni, Y. and Wang, X., "Mechanism of the Methanol based ClO_2 Generation Process", J. Pulp Paper Sci. **23:7,** J 346 (1997).

Rapson, R.H., Chem.Can., **18,** 25(1966).

Tang, T.F. and Gordon, G., "Quantitative Determination of Chloride, Chlorite and Chlorate in a Mixture by Successive Potentiometric Titrations", Anal.Chem., **52,** 1430 (1980).

Vogel, A.I., "Text Book of Quantitative Chemical Analysis", Longman, Inc., New York, 5th edition (1989) p. 390.

Woodside, V. and Macleod, K.S., "Chlorine Dioxide for Bleaching", Pap.Trade J., **26,** 137 (1953).

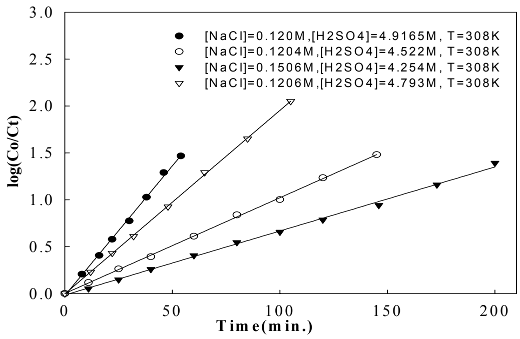

Fig. 1. First order dependence of chlorate conc.

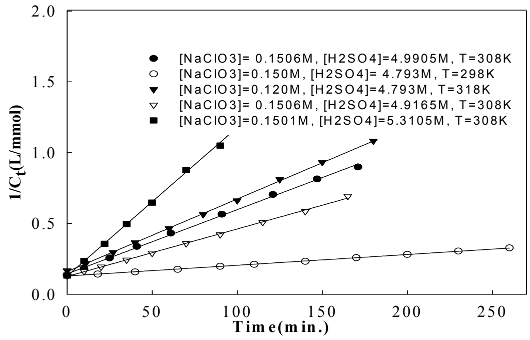

Fig. 2. Second order dependence of chloride conc.

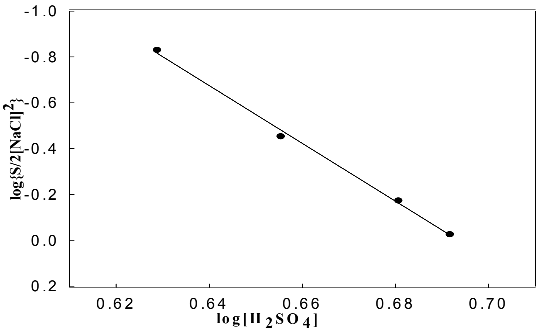

Fig. 3. Order w.r.t acid at constant chloride conc.

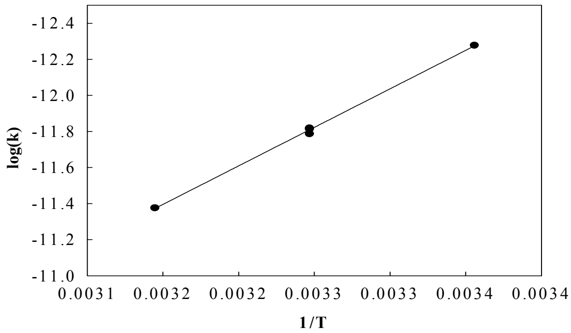

Fig. 4. Arrehenius Plot.

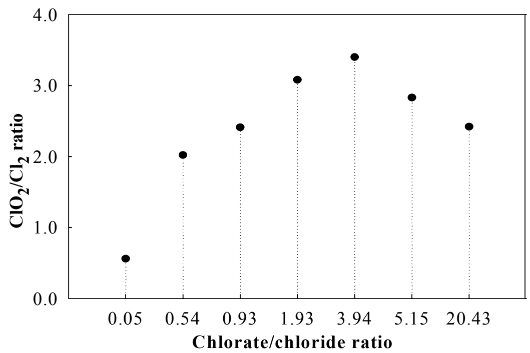

Fig.5. Effect of ClO_3^-/Cl^- ratio on ClO_2/Cl_2 ratio

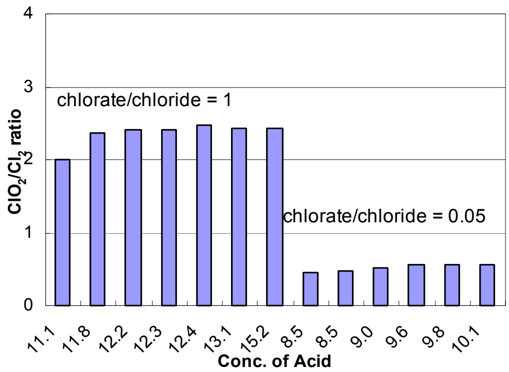

Fig. 6. Effect of conc. of acid on ClO_2/Cl_2 ratio

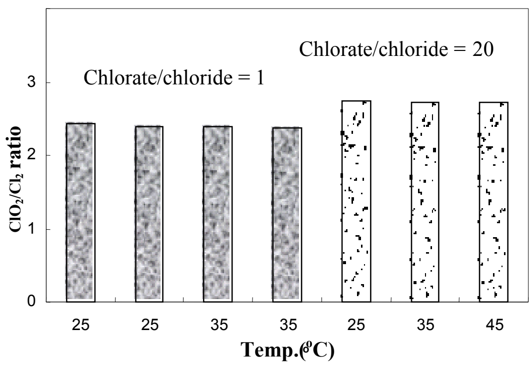

Fig. 7. Effect of temperature on ClO_2/Cl_2 ratio

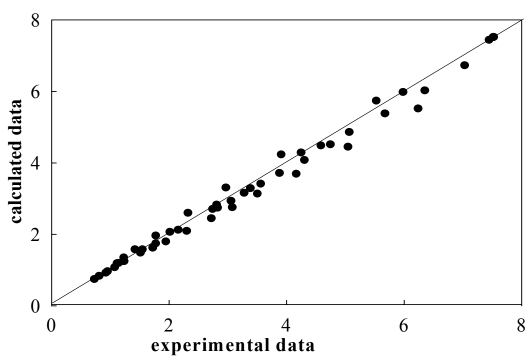

Fig. 8. Comparison of experimental and calculated data.