

NaClO₂ 분해속도에 관한 연구

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Study on Reaction Kinetics of the Decomposition of Acidic Sodium chlorite

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1. Introduction

Sodium chlorite has emerged as a new choice for bleaching textiles and paper pulp, wastewater treatment and air pollution control abatement. Its slightly acidic solution has been found to be a good absorbent for SO_x-NO_x because of its high absorption rate. When acidified in the absence of oxidizable material, chlorite yields mainly chlorine dioxide [Adewuyi et al., 1999; Yang and Shaw, 1998] which again is commercially used in water purification and as chemical bleach. The decomposition of chlorite in acid solution may produce both chlorine dioxide as well as chlorate. The rate of decomposition and reaction products is greatly influenced by experimental conditions, especially pH and presence of chloride.



The recent studies [Adewuyi et al., 1999; Yang and Shaw, 1998; Gordan, 1982] proposed that chlorite decomposition is catalyzed by the chlorides, which are invariably present either as an impurity or as the product of decomposition. Gordon [1982] proposed that the stoichiometry of the reaction alters in presence of chloride ion as follows:



Chloride plays crucial role in most of the ClO₂ generating processes. The present study is aimed to determine the rate constant, order of reaction with respect to chlorite as well as acid concentration and activation energy, so that the effect of concentration, temperature and pH can be well understood during the NaClO₂-HCl reaction. It will also be helpful to determine the optimum conditions to generate chlorine dioxide from acidic decomposition of sodium chlorite.

2. Materials and Methods

The experimental system is composed of a reactor and an absorber. Reactor is well stirred sealed vessel, fitted with pH control system. Continuous stirring was provided by a mechanical agitator. Temperature of the reaction vessel is controlled by water thermostat within ±0.1°C. Nitrogen gas was purged through chlorite solution using a bubbling device at a flow rate of one L/min. Chlorine dioxide carried by the nitrogen gas is absorbed in the absorber. The absorber consisted of 2 per cent KI solution, whose pH is controlled below 2.0 using pH control system by continuous addition of acid. Samples from reactor and absorber were titrated iodometrically against standard sodium thiosulfate solution using auto-titrator (Metrohm-Swiss).

Sodium chlorite (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 chlorite and chlorine dioxide. Chlorine dioxide absorbed in the absorber and chlorite left behind in the reactor were analyzed according to the standard methods [1989] and methods used by Aieta et al. [1984]. Sample from the reactor was also analyzed argentometrically for the initial concentration of chloride.

3. Results and discussion

The decomposition of sodium chlorite under acidic conditions was studied at various temperatures, pH and chlorite concentrations. The rate equation of reaction chlorite and acid was proposed as under:

$$\frac{dx}{dt} = k[\text{ClO}_2^-]^\alpha \times [\text{H}^+]^\beta \quad (3)$$

Where k is the rate constant, $[\text{ClO}_2^-]$ and $[\text{H}^+]$ are the concentrations and α , β are the order of reaction with respect to chlorite and acid respectively.

3.1. Concentration dependence

The concentration dependence of sodium chlorite was determined at different pH at 298K. Integration method was applied to determine the order of reaction with respect to chlorite. The graph plotted between $\ln(C_o/C_t)$ and time gave a straight line and the constancy in the value of k proved the first order dependence on chlorite. The first order dependence on chlorite concentration is shown in Figure 1.

The rate law can be expressed in terms of chlorite concentration as follows:

$$-\frac{1}{5} \frac{d[\text{ClO}_2^-]}{dt} = k[\text{ClO}_2^-]^\alpha \times [\text{H}^+]^\beta \quad (4)$$

Rearranging and integrating equation (4), it gives:

$$\ln(C_o/C_t) = 5 k [\text{H}^+]^\beta \times t \quad (5)$$

The slopes (S) of the straight lines of Fig. 1 can be written as:

$$S = 5 k [\text{H}^+]^\beta \quad (6)$$

Taking logarithm on the both sides, it yields:

$$\log S = \log(5 k) - (\beta \times \text{pH}) \quad (7)$$

So plotting graph between $\log S$ and pH, we obtained a straight line whose slope is equal to $(-\beta)$ i.e. order of reaction with respect to acid concentration. Figure 2 represents the pH dependence of the reaction rate wherein slopes of the straight lines are again different due different pH of the reaction. $\log S$ is plotted against pH in Figure 3. The slope of the straight line in Figure 3 is about one, which revealed the first order dependence on acid concentration.

3.2. Temperature dependence

Reaction kinetics was studied by performing experiments at different temperatures i.e. 15, 25, 35°C at fixed pH of 2.0. Rate constants at different temperatures were obtained from the slopes of straight lines in Figure 4. The Arrhenius plot of the rate constants is shown in the Figure 5. The value of activation energy ($E_a=37.75$ kJ/mol) is determined from slope and the pre-exponential frequency factor ($A=1.796 \times 10^6$) is determined from intercept of the straight line.

Therefore, the rate law for the decomposition of acidic sodium chlorite can be written as follows:

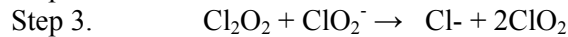
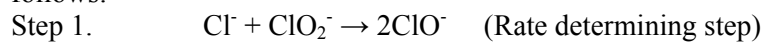
$$-\frac{1}{5} \frac{d[\text{ClO}_2^-]}{dt} = A \times \exp(-E_a / RT) \times [\text{ClO}_2^-] \times [\text{H}^+] \quad (8)$$

With this kinetic equation, chlorite as well as chlorine dioxide concentration can be calculated at any time. Figure 6 shows the good agreement of the experimental and calculated data. Based on the results, we conclude that rate equation describes the chlorite decomposition and chlorine dioxide production very well during the course of reaction.

3.3. Chloride promoted mechanism

It has been observed earlier [Adewuyi et al., 1999; Yang and Shaw, 1998; Gordan, 1982], that the chloride ions not only catalyze the acidic decomposition of chlorite but also alters the

stoichiometry of the reaction. In the view of above, a plausible mechanism has been suggested as follows:



The overall equation as shown in Eq. 2 is obtained by multiplying step 2 and 3 by two and adding into step. Rate determining step clearly explains the effect of chloride on the acidic decomposition of chlorite.

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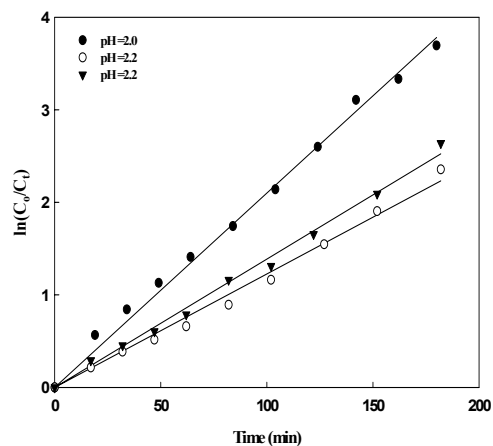


Fig. 1. 1st order dependence of chlorite concentration at 308K

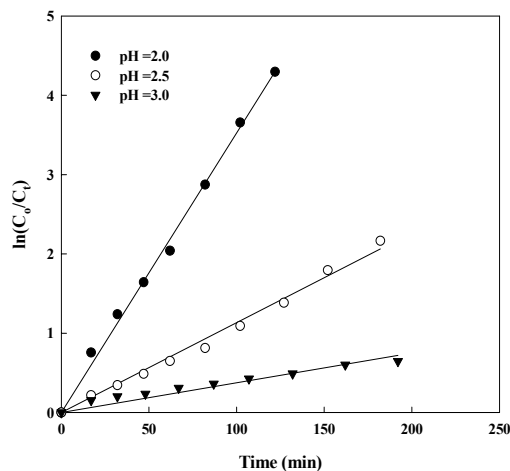


Fig. 2. Effect of pH on the reaction kinetics at different pH at 298K

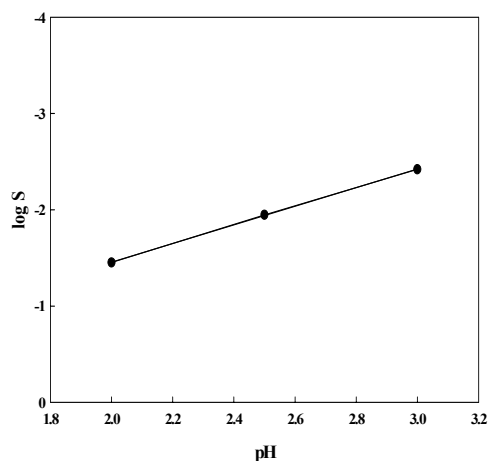


Fig. 3. 1st order dependence of acid concentration at 308K

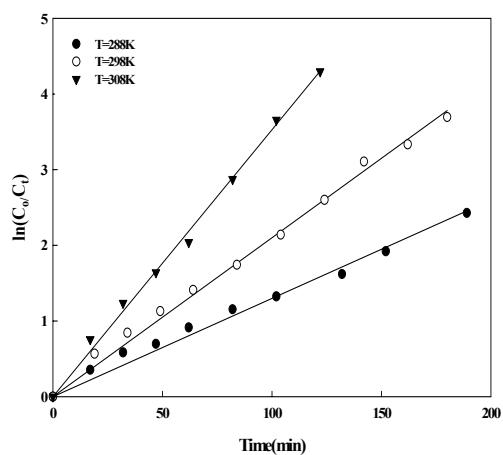


Fig. 4. Effect of temperature on reaction kinetics at pH of 2.0

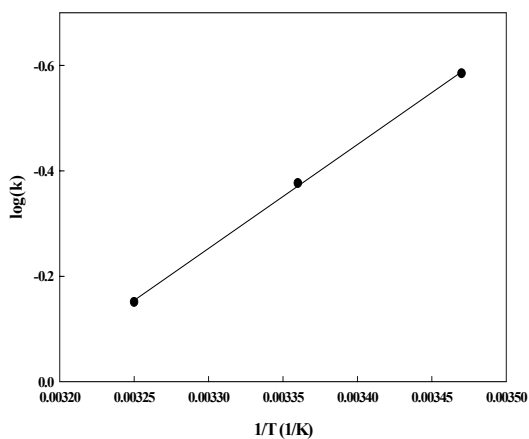


Fig. 5. Arrhenius plot of the rate constants

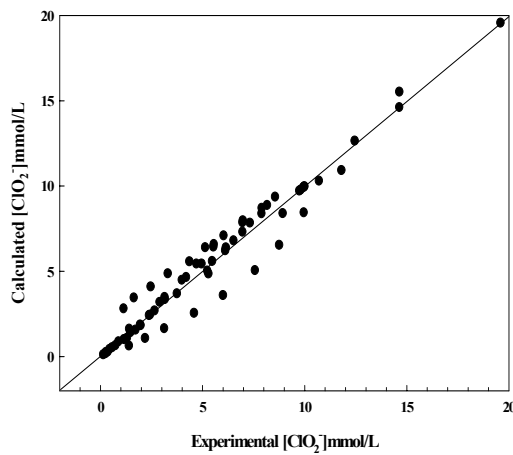


Fig. 6. Comparison of experimental and calculated data