

Kinetics of aniline oxidation with chlorine dioxide

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Abstract: For the first time, kinetics of aniline oxidation with chlorine dioxide (ClO₂) were investigated systematically by detecting concentration of aniline with HPLC at regular intervals. Results showed that the reaction was first-order both in ClO₂ and in aniline, and the oxidation reaction could be described as second-order reaction. Stoichiometric factor η was experimentally determined to be 2.44. The second-order-reaction rate constant k was 0.11 L/(mol·s) under condition of pH 6.86 and water temperature (T_w) 287K. Reaction activation energy was 72.31 kJ/mol, indicating that the reaction could take place under usual water treatment conditions. The reaction rate constants in acidic and alkali media were greater than that in neutral medium. Chlorite ion could slightly increase reaction rate in acidic medium. *p*-aminophenol and azobenzene were detected by GC-MS as intermediates.

Keywords: chlorine dioxide; aniline; kinetics

Introduction

ClO₂ is not only a broad-spectrum and persistent disinfectant but a strong oxidant as well. It reacts with organic pollutants generally as an electron acceptor and H atoms present in activated organic structures C-H or N-H are thereby not substituted by Cl. Compared with chlorine, it reacts with organic compounds to produce fewer chlorinated organic substances and no chloroform. Therefore, it has a broad application foreground in water treatment and international has recognized it as the most preferred fourth-generation disinfectant. Typical dosages of ClO₂ for drinking water treatment is 0.2—0.5 mg/L. Considering the low dosages and subsequently low residual concentration of ClO₂ (0.04—0.3 mg/L), a good understanding of the kinetics of ClO₂ reaction with organic contaminants in water is of great theoretical and engineering guiding value.

Aniline is an important raw material in pharmacy and dyeing. It is also an intermediate of pesticides degradation. Kinetics of reaction between ClO₂ and aniline had been studied by spectrophotometer analysis of ClO₂ (Feng, 1994). Since ClO₂⁻, ClO₃⁻ and ClO₂ without exception absorb UV to a different extent, the literature result was relatively inaccurate (Huang, 2000; Zhu, 2001). And COD variation cannot accurately characterize the aniline concentrations. Products of aniline oxidation vary with oxidants and reaction conditions. So far, there is little information about reaction mechanism of aniline oxidation with ClO₂ in literatures. For the first time, kinetics of the reaction between ClO₂ under water treatment conditions and aniline was systematically investigated by analysis of concentration variation of aniline with HPLC in this paper. And reaction mechanism was discussed preliminarily based on GC-MS detection result.

1 Materials and methods

1.1 Reagents and apparatus

(1) Reagents: Aniline, AR; ClO₂: prepared by reaction between sodium chlorite and vitriol followed by

saturated sodium chlorite washing. Purity of chlorine dioxide was above 99%; pH buffer solution was prepared by mixing NaH₂PO₄ and Na₂HPO₄ solution pro rata. All other reagents were of AR.

(2) Apparatus: HPLC was produced by Dalian Elite Analytical Apparatus Co., Ltd. with P200 II high-pressure and flux-controlled pump, UV200 II alterable wavelength detector and Echrom 98 chromatogram workstation. 78 ~ 1 magnetic beater.

1.2 General reaction rate law of aniline oxidation with chlorine dioxide

Reaction of aniline and chlorine dioxide can be described as follows:



η is the stoichiometric factor, $\eta = \Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2]$. Rate equation of the reaction is:

$$-d[\text{ArNH}_2]/dt = k[\text{ClO}_2]^m[\text{ArNH}_2]^n.$$

For the kinetic measurement initial concentration of chlorine dioxide $[\text{ClO}_2]_0$ was chosen to be at least ten times that of aniline $[\text{ArNH}_2]_0$, thus $[\text{ClO}_2]$ could be taken as invariable during the reaction (Jurg, 1994). To test for n and m alter the concentration of $[\text{ClO}_2]_0$ and $[\text{ArNH}_2]_0$ over a wide ranges and method of initial reaction rate was adopted. Stoichiometric factor η was determined by dividing the variation of $[\text{ClO}_2]$ by that of $[\text{ArNH}_2]$, that is

$$\eta = \Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2].$$

1.3 Research methods

1.3.1 Determination of reaction order and rate constant

Kinetics studies were conducted under a certain water temperature (T_w) in black receptacle to avoid photochemical complications as light accelerates reaction rate and decomposing of ClO₂. Solution of ClO₂, ArNH₂ and the quenching agent Na₂SO₃ were adjusted to the desired pH prior to the start of each experiment. Experiment procedure was as follows: add a certain volume of ArNH₂ solution with an injector into the reactor. Then start the beater and inject a certain volume of ClO₂ solution. At this time the volume of

the system was about 30 ml. Allow the reaction to proceed for a desired duration, and then terminate the reaction by addition of Na_2SO_3 . At the end of each experiment, the final pH of the system was measured. Drift in pH was unavoidable and the data reported in this paper are the initial pH measurement, which are considered most representative of the pH during the reaction. Then transfer all the solution in the reactor into a 100 ml separatory funnel. Extract this solution with benzene three times (10 ml for each time). And then combine the extraction. Sample with a mini-injector and determine the concentration of the residual aniline by means of HPLC. To determine the reaction order and the then rate constant was calculated. Initial reaction rate method was adopted.

1.3.2 Determination of stoichiometric factor

When $[\text{ArNH}_2] \rightarrow 0$, successive iodimetric technique was used to determine the concentration of residual chlorine dioxide $[\text{ClO}_2]$, thus the variation of chlorine dioxide $\Delta[\text{ClO}_2]$ was calculated. Took $\Delta[\text{ArNH}_2] = [\text{ArNH}_2]_0$, then $\eta = \Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2]$. When $[\text{ClO}_2] \rightarrow 0$, HPLC technique was used to determine the concentration of residual aniline $[\text{ArNH}_2]$. Took $\Delta[\text{ClO}_2] = [\text{ClO}_2]_0$, then $\eta = \Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2]$.

1.3.3 Study on reaction mechanism

Allow the reaction to proceed a desired duration under water treatment condition. Reaction intermediates were conformed by GC-MS. And reaction mechanism was preliminarily discussed.

1.4 Analytical methods

1.4.1 Determination of chlorine dioxide concentration

Concentration of ClO_2 was determined by successive iodimetric technique (Huang, 2000).

1.4.2 Determination of aniline concentration

Concentration of aniline was detected by HPLC. The chromatogram condition was: flowing phase: 85% methanol (chromatogram purity) solution; filling of separation column; Hyper ODS2 C18; length of the separation column: 250 mm; diameter of the separation column: 4.6 mm; flux: 1.0 ml/min; pressure: 5.00 MPa; sample volume: 10 μl ; wavelength of detector: UV254. Separation chromatogram under this condition is shown in Fig.1. Apex 3 was aniline and its retention time was 2.34 min. Apex 5 was benzene (introduced as extraction reagent for minimum aniline and inner criterion) and its retention time was 3.17 min. Other apices were products. It was evident that aniline was separated distinctively from the system.

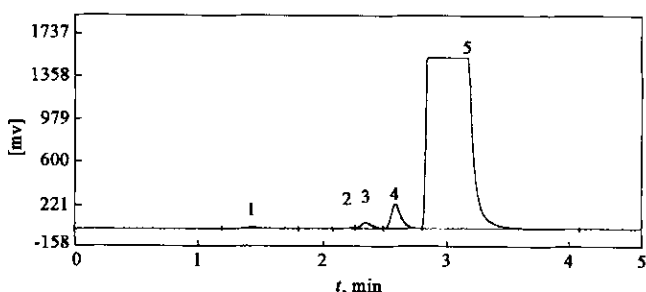


Fig.1 Separation chromatogram of aniline

2 Results and discussion

2.1 Standard curve of aniline

Standard curve of aniline is shown in Fig.2. Abscissa A was quotient of apex area of aniline and inner criterion (benzene). Regression equation of the standard curve was $C = 57.104A - 0.0198$ and the correlation coefficient was 0.9997.

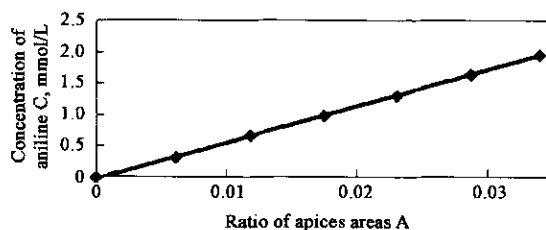


Fig.2 Standard curve of aniline

2.2 Kinetics results of reaction between aniline and chlorine dioxide

2.2.1 Reaction order in aniline

Initial concentration of chlorine dioxide $[\text{ClO}_2]_0$ was 0.01 mol/L. Reaction proceeded under condition of pH 6.86 and T_w 287 K. Effect of $[\text{ArNH}_2]_0$ on initial reaction rate v_0 is shown in Table 1.

It was revealed in Table 1 that v_0 was in direct ratio to $[\text{ArNH}_2]_0$ and the value of $(v_0 \times 10^3 / [\text{ArNH}_2]_0)$ was invariable, meaning that the reaction between aniline and ClO_2 was first order with respect to aniline, that is $n = 1$.

Table 1 Influence of $[\text{ArNH}_2]_0$ on v_0

$[\text{ArNH}_2]_0 \times \text{mol/L}$	$v_0 \times 10^6 \text{ mol}/(\text{L} \cdot \text{s})$	$v_0 \times 10^3 / [\text{ArNH}_2]_0, \text{ s}^{-1}$
0.0002	0.2000	1.0000
0.0005	0.5000	1.0000
0.0008	0.8000	1.0000
0.0010	1.0000	1.0000

Table 2 Influence of $[\text{ClO}_2]_0$ on v_0

$[\text{ClO}_2]_0, \text{ mol/L}$	$v_0 \times 10^6 \text{ mol}/(\text{L} \cdot \text{s})$	$v_0 \times 10^4 / [\text{ClO}_2]_0, \text{ s}^{-1}$
0.010	1.0000	1.0000
0.020	2.0000	1.0000
0.030	3.0000	1.0000

2.2.2 Reaction order in ClO_2

Initial concentration of aniline $[\text{ArNH}_2]_0$ was 0.001 mol/L. Reaction proceeded under condition of pH 6.86 and T_w 287 K. Effect of $[\text{ClO}_2]_0$ on initial reaction rate v_0 is shown in Table 2. Value of $(v_0 \times 10^3 / [\text{ClO}_2]_0)$ was invariable, illustrating that the reaction between aniline and ClO_2 was the first-order with respect to chlorine dioxide, that is $m = 1$.

2.2.3 Determination of the second-order-reaction rate constant

Based on the above experimental results, oxidation reaction of aniline with ClO_2 could be characterized as follows:

$$-d[\text{ArNH}_2]/dt = k[\text{ClO}_2][\text{ArNH}_2].$$

It can be integrated to be:

$$\ln([\text{ArNH}_2]_0/[\text{ArNH}_2]) = k[\text{ClO}_2]t.$$

Set $[\text{ClO}_2]_0 = 10[\text{ArNH}_2]_0 = 0.01 \text{ mol/L}$, then $[\text{ClO}_2]$ could be taken as invariable during the reaction (Jurg, 1999). Allow the reaction to proceed for regular intervals under condition of pH 6.86 and T_w 287 K. Concentration of aniline at each time interval was determined by HPLC analysis. Plot $\ln([\text{ArNH}_2]_0/[\text{ArNH}_2])$ vs t , slope was K_{obs} and $k = K_{\text{obs}}/[\text{ClO}_2]_0 = 0.0011/0.01 = 0.11 \text{ L}/(\text{mol} \cdot \text{s})$. Therefore, under condition of pH 6.86 and T_w 287 K, the second-order rate constant k of reaction between aniline and ClO_2 was $0.11 \text{ L}/(\text{mol} \cdot \text{s})$.

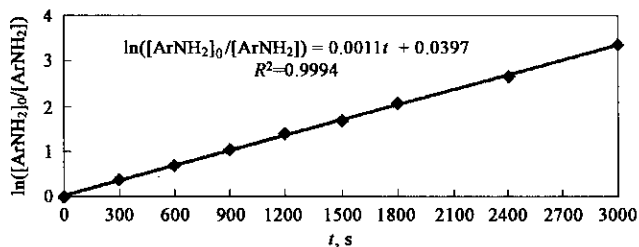


Fig. 3 Variation of $\ln([\text{ArNH}_2]_0/[\text{ArNH}_2])$ vs time

2.2.4 Determination of the stoichiometric factor

$[\text{ClO}_2]_0$ and $[\text{ArNH}_2]_0$ are set as in Table 3. Allow the reaction to proceed for such a long time that one of the reactants in the system disappeared under condition of pH 6.86 and T_w 287 K. $\Delta[\text{ClO}_2]$ and $\Delta[\text{ArNH}_2]$ were calculated as was described above, and $\eta = \Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2]$. Based on Table 3, $\eta = 2.44$.

Table 3 Stoichiometric factor of reaction

$[\text{ArNH}_2]_0, \text{ mol/L}$	$[\text{ClO}_2]_0, \text{ mol/L}$	$\Delta[\text{ClO}_2]/\Delta[\text{ArNH}_2], \eta$
0.0005	0.010	2.62
0.0010	0.010	2.54
0.010	0.0005	2.21
0.010	0.0010	2.38
Average	η	2.44

2.3 Effect of pH on the reaction rate constant

Solution pH changes not only the oxidation potential of ClO_2 but presence state of aniline in water as well. So pH was an important factor to affect reaction rate. Effect of pH on the reaction rate constant k is shown in Fig. 4.

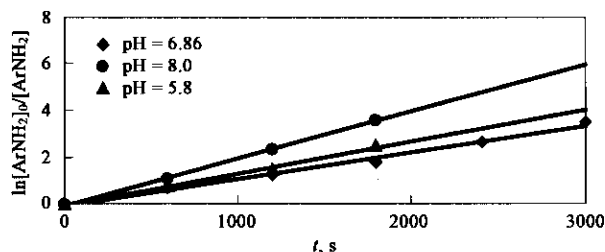


Fig. 4 Effect of pH reaction rate

$[\text{ClO}_2]_0 = 0.01 \text{ mol/L}$; $[\text{ArNH}_2]_0 = 0.001 \text{ mol/L}$; $T_w = 287 \text{ K}$
 pH = 6.86, $k = 0.11 \text{ L}/(\text{mol} \cdot \text{s})$; pH = 8.0, $k = 0.2 \text{ L}/(\text{mol} \cdot \text{s})$; pH = 5.8, $k = 0.13 \text{ L}/(\text{mol} \cdot \text{s})$

It was shown that reaction rate constants in acidic and alkali media were greater than that in neutral medium. Partial ClO_2 obtain 5 mol electrons to give Cl^- in acidic medium (pH

5.8). Thus oxidation potential of ClO_2 increased. Therefore, reaction rate constant increased. Accretion of the reaction rate constant in alkali system resulted from facilitation of aniline activation, which was in accordance with information in literature (Huang, 2002). Based on these results, it could be concluded that acidic and alkali media were favorable for the reaction to neutral condition.

2.4 Effect of ClO_2^- on reaction rate constant

In neutral and alkali media, ClO_2^- reacts hardly with aniline. But it can oxidize aniline in acidic medium. Under condition of $[\text{ClO}_2]_0 = 0.01 \text{ mol/L}$, $[\text{ArNH}_2]_0 = 0.001 \text{ mol/L}$, pH 5.8 and T_w 287 K, reaction rate constants were determined with different initial concentration of chlorite $[\text{ClO}_2^-]_0$. Results are as follows:

$[\text{ClO}_2^-]_0 = 0 \text{ mol/L}$, $k = 0.130 \text{ L}/(\text{mol} \cdot \text{s})$; $[\text{ClO}_2^-]_0 = 0.002 \text{ mol/L}$, $k = 0.137 \text{ L}/(\text{mol} \cdot \text{s})$; $[\text{ClO}_2^-]_0 = 0.010 \text{ mol/L}$, $k = 0.142 \text{ L}/(\text{mol} \cdot \text{s})$; $[\text{ClO}_2^-]_0 = 0.100 \text{ mol/L}$, $k = 0.144 \text{ L}/(\text{mol} \cdot \text{s})$.

Although ClO_2^- could oxidize aniline in acidic medium, addition of ClO_2^- to the system altered the reaction rate insignificantly. This maybe caused by the fact that rate of reaction ($\text{ClO}_2 + \text{ArNH}_2 \rightarrow \text{Cl}^- + \text{other products}$) is much faster than that of reaction ($\text{ClO}_2^- + \text{H}^+ + \text{ArNH}_2 \rightarrow \text{Products}$) under condition of pH 5.8.

2.5 Effect of temperature on reaction rate constant

To investigate effect of temperature, reaction rate constants with water temperature T_w 287 K, 293 K and 298 K respectively were determined under condition of $[\text{ClO}_2]_0 = 0.01 \text{ mol/L}$, $[\text{ArNH}_2]_0 = 0.010 \text{ mol/L}$ and pH 6.86. Results were as follows:

$k_{293\text{K}} = 0.206 \text{ L}/(\text{mol} \cdot \text{s})$; $k_{287\text{K}} = 0.11 \text{ L}/(\text{mol} \cdot \text{s})$;
 $k_{298\text{K}} = 0.337 \text{ L}/(\text{mol} \cdot \text{s})$.

Average activation energy $E = 29.87 \text{ kJ/mol}$ was calculated according to Arrhenius equation. This activation energy indicated that the oxidation of aniline by chlorine dioxide could take place under usual water treatment conditions (Cui, 2001).

2.6 Discussion of reaction mechanism

It was reported that reaction of ClO_2 with alcohol follows a hydride abstraction mechanism (Kudesia, 1981), and oxidation of phenol, aliphatic amines, olefins, and polycyclic aromatic hydrocarbon by ClO_2 follow single-electron-transfer mechanism (Rosenblatt, 1982; Huang, 2002; Cui, 2001; Chaim, 1986; Rav-Acha, 1985). As a result of the conjugation between the lone electron pair on the nitrogen and the π -bond of the benzene-cycle, the electron cloud of aniline is partially transferred to the benzene-cycle. Therefore, the concentration of the electron cloud is reduced on the nitrogen atom. And this makes the difference between aniline and aliphatic amines.

GC-MS technique was employed to determine intermediates of reaction between ClO_2 and aniline. *p*-aminophenol and azobenzene were detected as intermediates under water treatment conditions. It is known that reaction between ClO_2 and phenol followed single-electron-transfer mechanism. Reaction products of ClO_2 and phenol have been reported to be quinones and then simple organic and inorganic

acid (Huang, 2002; Wayon, 1982). Azobenzene was combining product of two aniline neutral radicals and which indicated the presence of this radical. Research has proved that azobenzene could be further degraded by ClO_2 (Deng,

1999). Based on the results of GC-MS and characteristics of the aniline molecule, possible pathways of reaction between ClO_2 and aniline were proposed in Fig.5.

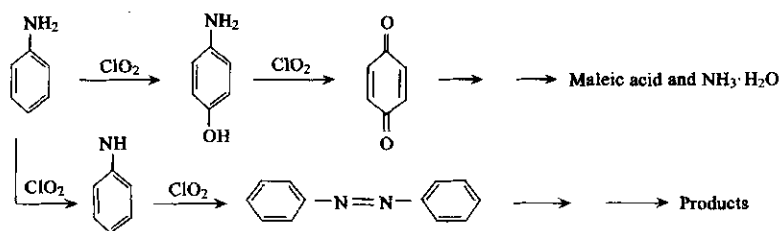


Fig.5 Proposed pathways of reaction between aniline and chlorine dioxide

3 Conclusions

Reaction between ClO_2 and aniline was the first-order with respect to both ClO_2 and aniline, and the overall reaction was of second order. The Stoichiometric factor η was 2.44. Under condition of pH 6.86 and T_w 287 K, the reaction rate constant k was $0.11 \text{ L}/(\text{mol} \cdot \text{s})$. Activation energy of the reaction was 72.31 kJ/mol , revealing that the reaction could take place under usual water processing conditions. Reaction rate constants in acidic and alkali media were greater than that in neutral medium. Therefore, acidic and alkali media were favorable for the reaction to neutral condition. In neutral and alkali media chlorite ion could hardly react with aniline. It could oxidize aniline in acidic medium, but the effect of it on the rate constant of reaction between ClO_2 and aniline was insignificant. The *p*-aminophenol and azobenzene were detected by GC-MS as intermediates.

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