



Kinetics and mechanisms of formation of earthy and musty odor compounds: Chloroanisoles during water chlorination



Kejia Zhang^a, Xinyan Zhou^a, Tuqiao Zhang^a, Minmin Mao^{a,b}, Lei Li^{c,*}, Wenchao Liao^d

^a College of Civil Engineering and Architecture, Zhejiang University, Hangzhou, 310058, Zhejiang, China

^b Urban Administration Bureau of West Lake District, Hangzhou, 310000, Zhejiang, China

^c State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai, 200092, China

^d School of Environmental Science and Engineering, Xiamen University of Technology, Xiamen, 361024, Fujian, China

HIGHLIGHTS

- Anisole can be chlorinated by HOCl to form chloroanisoles and para-products are more easily produced than ortho-products.
- Hydrogen ion can promote the reaction during the formation of chloroanisoles.
- Relative importance of factors in chloroanisole formation is: chlorine dose > initial anisole concentration > temperature.

ARTICLE INFO

Article history:

Received 6 June 2016

Received in revised form

6 August 2016

Accepted 9 August 2016

Available online 22 August 2016

Handling Editor: Xiangru Zhang

Keywords:

Chloroanisole

Chlorination

Kinetic model

Earthy and musty odor

ABSTRACT

Chloroanisoles are often reported as off-flavor compounds which produce an earthy and musty flavors and odors in drinking water. To improve understanding and ultimately minimize the formation of 2,4-dichloroanisole (2,4-DCA), 2,6-dichloroanisole (2,6-DCA) and 2,4,6-trichloroanisole (2,4,6-TCA), which have low odor threshold concentrations (OTC: 0.03–4 ng L⁻¹), a kinetic database for the chlorination of anisole was established by kinetic measurements. The results showed that HOCl reacted with anisole in acidic solution, with the hydrogen ion as an important catalyst. Quantification of product distribution of the produced chloroanisoles demonstrated that a chlorine attack in the para-position was favored over the ortho-position. A kinetic model was formulated, which permitted investigation of the relative importance of the chlorine dose and other water quality parameters including the concentrations of anisole and several metal ions, as well as temperature, on the product distribution of chloroanisoles. In general, high chlorine doses led to low concentrations of intermediates. The presence of ions such as Fe³⁺ and Al³⁺ facilitated the formation of chloroanisoles, but Zn²⁺ and Mn²⁺ did not. The kinetic model can be applied to optimize water chlorination and minimize earthy and musty odors.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Chlorine is widely used for the chemical disinfection of drinking water because of its effectiveness, low cost, and general availability. However, as a disinfectant, chlorine can also react with natural organic matter (NOM) in source waters to produce disinfection by-products (DBPs) in drinking water that have the potential to cause cancer and reproductive problems (Richardson, 2011; Yang and Zhang, 2016). As a result, significant concern is associated with the health risks of drinking water quality, and little attention has

been paid to the off-flavor properties of treated water (Brosillon et al., 2009). However, drinking water must also have favorable taste and odor properties, because water quality is assessed by many consumers in terms of these properties. Therefore, a better understanding of the chemical cause of drinking water odors is necessary for water operators. The composition of water before the addition of chlorine has a great influence on DBP formation. In previous studies, 2,4,6-trichloroanisole (2,4,6-TCA) has been identified as the musty/muddy off-flavor in drinking water after chlorination. In Sweden, the 2,4,6-TCA concentration of lake water on five occasions were varied between 0.5 and 2.0 ng L⁻¹ (Nystrom et al., 1992). Mao et al. (2013) detected 5.86 ng L⁻¹ of 2,4,6-TCA in effluent at the end of a water distribution system. Because the odor threshold concentration of 2,4,6-TCA is extremely low at

* Corresponding author.

E-mail address: lilei87296281@126.com (L. Li).

0.03 ng L⁻¹ for water (Varelas et al., 2011), it can be easily detected by consumers. In addition to its effects on flavor, 2,4,6-TCA – as an aromatic halogenated DBP – has toxicological effects. In recent years, several studies have investigated toxicities of some aromatic halogenated DBPs including haloquininones, chlorophenazines, halophenolic compounds, and so on (Bull et al., 2011; Liu and Zhang, 2014; Pan et al., 2016). Numerous researchers have indicated that 2,4,6-TCA is produced by the biomethylation of 2,4,6-trichlorophenol (2,4,6-TCP), which is the precursor of 2,4,6-TCA, by several varieties of bacteria and fungi in wine (Miki et al., 2005; Mazzoleni and Maggi, 2007; Park et al., 2007; Haas et al., 2010).

However, the mechanisms underlying the 2,4,6-TCA formation in water are uncertain, and it is surmised to be produced by the chlorination of anisole with chlorine. Anisole is an off-flavor compound widely used in industry, and can therefore be commonly detected in the environment including in surface waters. As a 2,4,6-TCA precursor, anisole can be chlorinated to form 2,4,6-TCA even at low concentrations. Further, because of its low molecular weight and formation after the last treatment of step-disinfection, 2,4,6-TCA is not effectively removed in water works.

To minimize the existence of 2,4,6-TCA, its formation needs to be explained firstly. The purpose of the study is therefore to investigate the formation of 2,4,6-TCA and other chloroanisoles with unpleasant odors (Varelas et al., 2011) including 2-chloroanisole (2-CA), 4-chloroanisole (4-CA), 2,4-dichloroanisole (2,4-DCA), and 2,6-dichloroanisole (2,6-DCA), whose odor threshold concentrations are 1–50 ng L⁻¹ (Fischer and Fischer, 1997). This is a complicated problem because the behavior of these compounds can differ significantly depending on source water quality and chlorination conditions. Therefore, in this study, the chlorination of anisole-containing water to produce chloroanisoles under different pH will be investigated. Further, because the chlorine dose in water treatment varies from 1.0 to 2.5 mg L⁻¹ (Yan and Fan, 1999), the chlorination reaction of anisole will be investigated here under various chlorination levels. Reactions at several temperatures will also be studied to simulate water treatment temperatures for different seasons, and four metal ions (Al³⁺, Fe³⁺, Mn²⁺, Zn²⁺) – which are typically found in natural waters in great abundance – are included to investigate their effects on the chloroanisole formation. Finally, this study also demonstrate the formation of chloroanisoles kinetics and propose a statistical model to describe and predict the conversion of chloroanisoles.

2. Materials and methods

2.1. Chemicals

Standards of the target analytes including anisole, 2-CA, 4-CA, 2,4-DCA, 2,6-DCA and 2,4,6-TCA were purchased from Sigma-Aldrich (US). The internal standard 2-isobutyl-3-methoxy-pyrazine (IB, 99%) was purchased from Fluka (Japan). Sodium hypochlorite (Sinopharm Chemical Reagent Co., 5.2% available chlorine) was used as the chlorine source. Other analytical grade reagents, including NaCl, Na₂S₂O₃, AlCl₃, ZnCl₂, FeCl₃, MnCl₂, NaOH, HCl were obtained from Sinopharm Chemical Reagent Co., China. NaCl was heated to 450 °C for 2 h before use. The actual concentration of chlorine was determined prior to each experiment, using a free chlorine powder pillow reagent (HACH) and a DR2800 ultraviolet spectrophotometer (HACH, US).

2.2. Experimental procedure

Chlorination experiments were carried out in 150 mL amber glass bottles with Teflon-faced septa placed in a constant temperature incubator (SPX-250B-Z). Before each experiment, 100 mL of

anisole solution of a known concentration was added to a bottle, and a volume of sodium hypochlorite stock solution (2.4 g L⁻¹ available chlorine) was added to the solution, to ensure surplus chlorine concentration over the entire experiment. The pH of the solution for each experiment was adjusted to a chosen value using HCl or NaOH. In the metal ions experiments, the molar ratio of anisole to the cation (Fe³⁺, Al³⁺, Mn²⁺ or Zn²⁺) was 1:1. At each designated sampling time, one amber glass bottle was used for analysis. After sodium thiosulfate was added to quench chlorination, a 100 mL sample was collected for chloroanisoles analysis.

2.3. Analysis

Anisole, 2-CA, 4-CA, 2,4-DCA, 2,6-DCA and 2,4,6-TCA were quantified using solid phase micro-extraction (SPME) coupled with GC (QP2010, Shimadzu, Japan)-MS (QP2010 plus, Shimadzu, Japan). The detailed procedures for SPME are available in previous publications (Zhang et al., 2011). The GC operational conditions were as follows. A RTX-5MS capillary column (30.0 m × 0.25 mm × 0.25 μm) was used. The carrier gas was high purity helium (>99.999%, Jingong Corp., China) at a pressure of 90 kPa. The injection port was operated in a splitless mode with a controlled temperature of 250 °C. The oven temperature program was initially set at 60 °C for 3 min, increased at a rate of 6 °C/min to 150 °C, increased at a rate of 15 °C/min up to 250 °C, and finally maintained at 250 °C for 3 min. The MS operational conditions were as follows. The MS ion source temperature was set at 200 °C. The intermediate species and 2,4,6-TCA during the chlorination of anisole were identified using scan mode at *m/z* from 45 to 500.

Matlab 7.0 (MathWorks) and Origin 8.5 (OriginLab) were used to develop the kinetic models applied in Section 3.1.3. SPSS was used to calculate the linear relationship between three effects in Section 3.6.

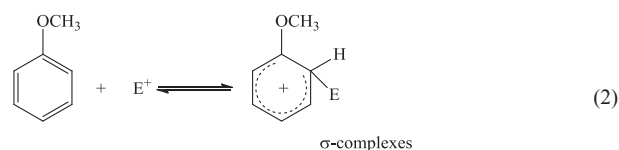
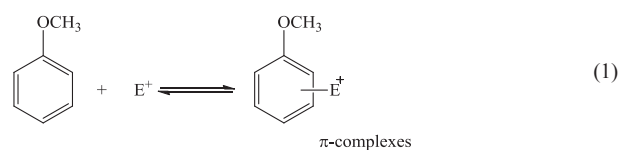
All experiments and sampling were conducted in triplicate and all data were represented by average values.

3. Results and discussion

3.1. Formation pathway of chloroanisoles

3.1.1. Formation of chloroanisoles under acid conditions

Chlorination of anisole is a typical electrophilic substitution and there are generally three main steps in the reaction process. (1) An electrophile (E) attacks a benzene ring to form a π-complexes and retains the benzene ring structure. (2) The electrophile in the π-complexes attaches to one of the carbon atoms of the benzene ring and changes to σ-complexes. (3) A hydrogen atom bonded with benzene ring detaches and produces H⁺. This process could be described as Eqs. (1)–(3) (Ge et al., 2006).



Download English Version:

<https://daneshyari.com/en/article/6306260>

Download Persian Version:

<https://daneshyari.com/article/6306260>

[Daneshyari.com](https://daneshyari.com)