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Determination of rapid chlorination rate constants by a stopped-flow spectrophotometric competition kinetics method

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ABSTRACT

Free chlorine is extensively used for water and wastewater disinfection nowadays. However, it still remains a big challenge to determine the rate constants of rapid chlorination reactions although competition kinetics and stopped-flow spectrophotometric (SFS) methods have been employed individually to investigate fast reaction kinetics. In this work, we proposed an SFS competition kinetics method to determine the rapid chlorination rate constants by using a common colorimetric reagent, N,N-diethyl-*p*-phenylenediamine (DPD), as a reference probe. A kinetic equation was first derived to estimate the reaction rate constant of DPD towards chlorine under a given pH and temperature condition. Then, on that basis, an SFS competition kinetics method was proposed to determine directly the chlorination rate constants of several representative compounds including tetracycline, ammonia, and four α-amino acids. Although Cl_2O is more reactive than HOCl, its contribution to the overall chlorination kinetics of the test compounds could be neglected in this study. Finally, the developed method was validated through comparing the experimentally measured chlorination rate constants of the selected compounds with those obtained or calculated from literature and analyzing with Taft's correlation as well. This study demonstrates that the SFS competition kinetics method can measure the chlorination rate constants of a test compound rapidly and accurately.

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1. Introduction

Chlorine is the most widely used chemical disinfectant around the world. It is cheap, stable and effective against many pathogens including bacteria and viruses. Hence, despite the formation of harmful chlorinated disinfection byproducts, chlorine will still act as a primary disinfectant in many countries. In recent years, the transformation and fate of various organic micropollutants during water chlorination have attracted increasing attentions (Deborde and von Gunten, 2008; Sharma, 2008; Sedlak and von Gunten, 2011). As a prerequisite, the kinetic rate constants of a micropollutant reacting towards chlorine should be determined,

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so as to predict the removal efficiency and identify the primary reaction sites of the micropollutant under certain experimental conditions (Gallard and von Gunten, 2002; Li and Zhang, 2012). However, the kinetic study presents a great challenge for researchers because the reaction between chlorine and an organic micropollutant generally proceeds sufficiently fast to preclude measurement by conventional batch/quench techniques.

Competition kinetics method, by using a reference compound whose rate constant towards a specific oxidant is already known, has been developed for kinetic study of many fast reactions (Acero et al., 2010; Wang et al., 2011). In this method, a test compound and a reference compound are simultaneously oxidized in an aqueous solution, and then their residual concentrations at pre-selected time intervals are quantified after instrumental separation (e.g., using liquid chromatography or gas chromatography techniques). By comparing to the available rate constant of the reference compound towards the applied oxidant, the rate constant of the test compound can be calculated. However, the frequent operations such as sample withdrawal, pretreatment, separation, and analysis are not only time-consuming but also labor-intensive. Stopped-flow spectrophotometric (SFS) method, which permits immediate and continuous observations of a fast reaction, appears to be a promising technique for studying fast reaction kinetics in an aqueous solution if there is no spectral interference between the reactants and the products (Qiang and Adams, 2004; Karnas et al., 2010).

It is well known that a commonly used colorimetric reagent, *N*,*N*-diethyl-*p*-phenylenediamine (DPD), can react rapidly with chlorine to yield a stable semi-quinoid cationic radical ($DPD^{\bullet+}$) called "Würster dye". This cationic radical has a strong absorbance at 510 nm, where no spectral interference from most compounds can be observed (Michaelis, 1931; Zarei and Sovizi, 2011). Hence, this reaction has been adopted to determine aqueous chlorine concentration by a standard method (APHA, 1998; Moberg and Karlberg, 2000).

In the present study, a kinetic equation was first derived to estimate the reaction rate constants between chorine and DPD over a pH range of 6.75–8.90 and a temperature range of 18–37 °C, which are quite representative for water and wastewater treatment. Then, by using DPD as a reference probe, an SFS competition kinetics method was developed to determine directly the chlorination rate constants of tetracycline (TCN), ammonia, and four α-amino acids. Finally, this developed method was validated through comparison of the experimentally determined chlorination rate constants of the selected compounds with those obtained from literature and through Taft's correlation analysis as well.

2. Materials and methods

2.1. Chemicals

All chemicals were at least of analytical grade and used as received. Sodium perchlorate, sodium borate, boric acid, ammonium chloride, glycine, and valine were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Alanine and leucine were purchased from Biosharp (Hefei, China), DPD from Alfa Aesar China Co., Ltd. (Tianjin, China), and TCN from Jing Ke Hong Da Biotechnology Co., Ltd. (Beijing, China). Sodium hypochlorite (NaOCl, >10% available chlorine), supplied by Beijing Chemical Co. (Beijing, China), was used as the source of free chlorine (FC) and periodically standardized by a DPD colorimetric method (Li et al., 2007) with a UV–Visible spectrophotometer (Hitachi U-3010, Japan). Ultrapure water was produced by a Millipore Water Purification System (Advantage A10, Millipore) with a resistivity of ≥18.2 MΩ cm. This ultrapure water was used to prepare all reaction solutions in this study. The working solutions of DPD and NaOCl were freshly prepared every day and stored in amber bottles to prevent possible degradation by light. Sodium borate and boric acid were used as buffer to control the solution pH in the range of 6.75–8.90. An Orion 720A digital pH meter coupled with a combinational pH electrode (Thermo Scientific Inc., US) was used to measure the solution pH.

2.2. Experimental procedures

A stopped-flow spectrophotometer (Model SX20, Applied Photophysics Ltd., Leatherhead, UK) was used to conduct kinetic experiments. The temperature of the reaction solution was controlled by an automatic water circulator (Thermo Fisher Scientific, Waltham, MA) connected to the stopped-flow's sample handling unit. An HP computer workstation was employed to control the stopped-flow and acquire the kinetic data as well. Kinetic traces were analyzed by the Pro-Data software from Applied Photophysics Ltd. Unless otherwise stated, all kinetic experiments were carried out in triplicate at 24 ± 1 °C.

For the kinetic experiments, an equal volume of DPD and NaOCl solutions was simultaneously injected into the optical cell of the stopped-flow with two automatic syringes driven by compressed air. The DPD concentration was kept in at least 10-fold excess of NaOCl concentration to simulate the pseudo-first-order reaction conditions. In a typical experiment, 0.20 mM DPD and 0.01 mM NaOCl were employed. All reaction solutions were buffered with 10 mM borate and adjusted to a desired pH, and the ionic strength was controlled with 50 mM $NaClO_4$. The formation of $DPD^{\bullet+}$ was continuously monitored at 510 nm to determine the pseudo-first-order reaction rate constant. The second-order rate constant was then obtained by dividing the pseudo-first-order rate constant by the initial concentration of DPD.

The competition kinetics experiments were performed under the same experimental conditions as above (e.g., 10 mM borate buffer, 50 mM $NaClO_4$ for ionic strength control). TCN, ammonia, and four α-amino acids were selected for chlorination tests. One working solution contained a test compound of varied concentrations and the reference compound (DPD, 0.20 mM), and the other contained 0.01 mM NaOCl solution. The two working solutions were simultaneously injected into the stopped-flow's optical cell through two automatic syringes and the reaction was initiated immediately. Because the test compound was able to compete for chlorine against DPD, the formation rate of $DPD^{\bullet+}$, as denoted by the 510 nm absorption peak, would slow down. Zero-point correction was applied to each kinetic trace to obtain an absolute absorbance change, which reflected the fraction of chlorine consumed by

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