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# Short Communication Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI)

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## 1. Introduction

Sucralose (4-chloro-4-deoxy- $\alpha$ -D-galactopyranosyl-1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside) is a chlorinated derivative of the disaccharide sucrose; in which three hydroxyl groups are replaced by chlorine atoms (Fig. 1). Sucralose is about 600 times sweeter by weight than sucrose (Wiet and Miller, 1997). The use of sucralose is widespread in over 80 countries and it is present in more than 4000 different products (Torres et al., 2011). For example, sucralose is being used as a non-nutritive sweetener in the sugar substitute known commercially as SPLENDA, which contains  ${\sim}1\%$  sucralose and 99% maltodextrin and dextrose in the granulated product. The human consumption of sucralose has been found safe (Grotz and Munro, 2009), however, it is also considered an emerging contaminant due to its persistence in the environment, with a half-life of up to several years (Lubick, 2008; Richardson and Ternes, 2011). Recently, several studies have determined sucralose concentrations up to  $1 \ \mu g \ L^{-1}$  in river, coastal, and marine waters of North America and Europe (Loos et al., 2009; Lubick, 2009; Mead et al., 2009). The input of sucralose to the environment is likely through municipal wastewater treatment effluents (Torres et al., 2011). The present study thus sought the removal of sucralose by ferrate(VI) ( $FeO_4^{2-}$ , Fe(VI)) in order to minimize release of this emerging contaminant to aquatic ecosystems.

#### ABSTRACT

The kinetics of the oxidation of sucralose, an emerging contaminant, and related monosaccharides and disaccharides by ferrate(VI) (Fe(VI)) were studied as a function of pH (6.5–10.1) at 25 °C. Reducing sugars (glucose, fructose, and maltose) reacted faster with Fe(VI) than did the non-reducing sugar sucrose or its chlorinated derivative, sucralose. Second-order rate constants of the reactions of Fe(VI) with sucralose and disaccharides decreased with an increase in pH. The pH dependence was modeled by considering the reactivity of species of Fe(VI), (HFeO<sub>4</sub><sup>-</sup> and FeO<sub>4</sub><sup>2-</sup>) with the studied substrates. Second-order rate constants for the reaction of Fe(VI) with monosaccharides displayed an unusual variation with pH and were explained by considering the involvement of hydroxide in catalyzing the ring opening of the cyclic form of the carbohydrate at increased pH. The rate constants for the reactions of carbohydrates with Fe(VI) were compared with those for other oxidant species used in water treatment and were briefly discussed. © 2012 Elsevier Ltd. All rights reserved.

There have been several studies on the novel properties of Fe(VI) as an oxidant, disinfectant, and coagulant (Eng et al., 2006; Jiang, 2007; Lee et al., 2009; Sharma et al., 2009; Sharma, 2010a; Sharma et al., 2010), but no data has been published on rate constants for the oxidation of sucralose or any carbohydrate by Fe(VI). In this paper, the kinetics of the reactions between Fe(VI) with sucralose and carbohydrates were determined as a function of pH (6.5-10.1) at 25 °C. Structures of the selected carbohydrates are shown in Fig. 1. The kinetic study of sucrose provided an interesting comparison with that of sucralose. Sucrose, also known as table sugar, is a disaccharide of D-glucose and D-fructose. Therefore, the six-carbon monosaccharides glucose and fructose were also chosen for this study. D-Glucose, also called dextrose, was found to be the most abundant sugar in groundwater (Spitzy, 1982). D-Fructose is an isomer of glucose (Fig. 1). Another carbohydrate of interest in this study is the disaccharide maltose containing two D-glucose units. Carbohydrate-type structures are also found in humic substances (Canellas et al., 2010) and the results of the present study may thus have implications in reducing levels of humic substances by reaction with Fe(VI).

The objectives of the study were: (i) to determine rate laws and rate constants for the oxidation of sucralose and various related carbohydrates by Fe(VI); (ii) to compare the rate constants of the carbohydrates with Fe(VI) to each other to see if differences in rate constants can be related to structural differences. This should allow for better predictions to be made regarding the reactivity of Fe(VI) with a greater variety of carbohydrates and (iii) to understand the pH dependence of the oxidation of carbohydrates by Fe(VI) in order to expand the relevance of the results to a greater variety of environmental conditions.





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Fig. 1. Structures of studied carbohydrates and sucralose.

#### 2. Experimental approach

All glassware used in this study was soaked overnight in 50% nitric acid and rinsed thoroughly with distilled water before use. All solutions were prepared in water which had been distilled and then further purified through a Milli-Q system (18.2 M $\Omega$  cm). A solution of ~200  $\mu$ M Fe(VI) was prepared by dissolving solid potassium ferrate(VI) (K<sub>2</sub>FeO<sub>4</sub>) (purity > 98%) into a 5 mM Na<sub>2</sub>HPO<sub>4</sub>/ 1 mM borate ((Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>•10H<sub>2</sub>O) buffer solution at pH 9.0 (Luo et al., 2011). Substrate solutions were prepared in 0.01 M phosphate buffer in a concentration range of 0.05–0.25 M. This concentration range was selected based on the desire to maintain substrate concentrations at least ten times greater than ferrate concentrations for pseudo-order conditions to perform kinetics measurements. The pH of the substrate solution was adjusted by adding either concentrated phosphoric acid or sodium hydroxide solution.

All kinetic studies were performed on a stopped-flow spectrophotometer (SX-18 MV, Applied Photophysics, UK) with a photomultiplier detector. Time spectra were collected in the wavelength range from 350 to 750 nm. Kinetic traces were collected at a wavelength of 510 nm to determine the pseudo-first-order rate constants using solutions in which the substrate was in excess. Stopped flow experimental data was analyzed using the nonlinear least-square algorithm of the SX-18MV global software (Applied Photophysics, UK). Rate constants reported represent the average of six replicate runs. The spontaneous self-decay rate of Fe(VI) was measured under conditions identical to the experimental oxidation conditions to allow for a correction in the rate constant. Routine spectral measurements were performed on an Agilent Model 8453 UV–Vis spectrophotometer.

## 3. Results and discussion

Initially, the reactivity of Fe(VI) with monosaccharides was studied at pH 9.0 and 25 °C. The spectral measurements for monitoring the reactions are shown in Fig. SM-1 and indicate the decay of Fe(VI) without any suggestion of the formation of any

intermediate(s) such as Fe(VI)-carbohydrate complexes. The complexation of carbohydrates with high-valent chromium species has been observed (Roldán et al., 2002; Codd et al., 2003; García et al., 2006), however it appears that the oxidation of monosaccharides by Fe(VI) occurred without precursor complexation for the time scale of the studied reactions. Similar results were observed for the reactions of Fe(VI) with disaccharides and with sucralose (Fig. SM-2).

The rates of the reactions were followed at 510 nm at different concentrations of substrates (S) under pseudo-first order conditions at pH 9.0. The insets of Figs. SM-1 and SM-2 show the decrease in absorbance of Fe(VI) with time, which fit nicely to single exponential decays. This suggests that the reactions are first-order with respect to the concentration of Fe(VI). The pseudo-first-order rate constants (k') were obtained at different concentrations of monosaccharides, disaccharides, and sucralose. A plot of k' versus concentration of substrate ([S]) consistently showed linear relationships (Fig. 2). A log-log plot of the data from Fig. 2 was constructed to obtain order with respect to the concentration of substrate (n) (Fig. SM-3). Slopes of the plot were nearly unity (Table 1); indicating the reaction is also first-order with respect to the concentration of substrate. The rate law is represented by the following equation:

$$-d([Fe(VI)])/dt = k[Fe(VI)][S]$$
(1)

where *k* is the second-order rate constant for the reaction of Fe(VI) with substrate. The values of *k* obtained at pH 9.0 are given in Table 1. The values of *k* did not span a large range varying from  $1.0 \times 10^{-1}$  to  $2.5 \times 10^{-1}$  M<sup>-1</sup> s<sup>-1</sup>. The slowest rate constants in this study were those for sucrose and sucralose (Table 1). Maltose had the highest rate constant (Table 1). The order of reactivity for monosaccharides was fructose > glucose while maltose > sucralose > sucrose was the order of reactivity for disaccharides.

Of the carbohydrates studied here, only sucrose is classified as a non-reducing sugar. Carbohydrates which can be oxidized by mild oxidizing agents such as Fe(III) or Cu(II) are referred to as reducing sugars (Nelson and Cox, 2005). The oxidation of sugars with Fe(III) Download English Version:

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