1. Introduction

Sucralose (4-chloro-4-deoxy-α-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 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; Lee et al., 2009; Sharma et al., 2010). The kinetics of 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.
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 MΩ cm). A solution of ~200 μM Fe(VI) was prepared by dissolving solid potassium ferrate(VI) (K₂FeO₄) (purity > 98%) into a 5 mM Na₂HPO₄/NaH₂PO₄ 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-first-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 (k₀) were obtained at different concentrations of monosaccharides, disaccharides, and sucralose. A plot of k₀ 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:

$$-\frac{d[Fe(VI)]}{dt} = k[Fe(VI)][S]$$

(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 × 10⁻¹ to 2.5 × 10⁻¹ M⁻¹ s⁻¹. 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)
or Cu(II) occurs at the anomeric carbon and only the linear form of the carbohydrate is reactive, not the cyclic form which is in equilibrium with the linear form. When two monosaccharides combine to form a disaccharide, a glycosidic bond forms as the hydroxyl group of one molecule reacts with the anomeric carbon of the other molecule (see Fig. 1). Sucrose, a disaccharide formed by the bonding of glucose and fructose has no free anomeric carbons since both are involved in the glycosidic bond. Thus sucrose is classified as a non-reducing sugar, e.g. it is not oxidized by either Fe(III) or Cu(II). Sucralose, its chlorinated derivative would also be expected to show similar behavior. All of the other substrates used in this study (glucose, fructose, and maltose) are classified as reducing sugars and are relatively easier to oxidize by Fe(VI) than are sucrose and sucralose (Table 1).

The $k$ values for the reaction of Fe(VI) with substrates were then determined at different pHs (Fig. 3). Generally, the $k$ values increased with decrease in pH (Fig. 3a and b), similar to results from most studies with Fe(VI) (Sharma et al., 2011; Sharma, 2011). However, the reactions of glucose and fructose with Fe(VI) showed unusual pH dependence behavior in which rates slightly increased with increasing pH (pH >8; Fig 3a). The variation in the $k$ values with pH in Fig. 3 can be explained by considering reactions between acid–base species of Fe(VI) \( \text{H}_2\text{FeO}_4 = \text{H}^+ + \text{H}_2\text{FeO}_4, \ \text{pK}_{a1} = 1.9; \ \text{H}_2\text{FeO}_4 = \text{H}^+ + \text{HFeO}_4, \ \text{pK}_{a2} = 3.5; \ \text{HFeO}_4 = \text{H}^+ + \text{FeO}_4^{\text{2}\text{-}}, \ \text{pK}_{a3} = 7.23 \) (Sharma et al., 2001) and substrates. In the pH range studied, substrates do not exhibit more than one pH-dependent species, hence the pH dependence of $k$ for the reaction of Fe(VI) was modeled using only two reactions (Eqs. (2) and (3)).

$$\text{HFeO}_4^- + S \rightarrow \text{Fe(III)} + \text{product(s)}$$

$$\text{FeO}_4^{\text{2}\text{-}} + S \rightarrow \text{Fe(III)} + \text{product(s)}$$

The more highly protonated species of Fe(VI), \( \text{H}_2\text{FeO}_4^- \) and \( 2\text{FeO}_4^{\text{2}\text{-}} \) were not considered because their $pK_a$ values are much lower than the pH of this study and contributions of these species would be negligible. The rate constant can thus be expressed as

$$k[\text{Fe(VI)}] = k_2[\text{HFeO}_4^-] + k_3[\text{FeO}_4^{\text{2}\text{-}}]$$

where $k_2$ and $k_3$ are the species-specific rate constants for reactions (2) and (3), respectively. The expression for $k$ can be simplified to Eq. (5) using an equilibrium expression for Fe(III) species

$$k = k_2\{[\text{H}^+]/[\text{K}_{a3} + [\text{H}^+])\} + k_3\{[\text{K}_{a3}/([\text{K}_{a3} + [\text{H}^+])\}$$

Values of $k_2$ and $k_3$ were determined using Eq. (5) by fitting the experimentally determined values of $k$ at different pH. Estimated values of species-specific rate constants are given in Table 1 for disaccharides, which fit reasonably well with the experimental results (solid lines, Fig 3b). The rate constants for the reaction of HFeO$_4^-$ were greater for disaccharides than for FeO$_4^{2-}$, which confirms results from earlier studies which indicate that monoprotonated species of Fe(VI) react faster with substrates than do unprotonated species of Fe(VI) (Sharma, 2010b). Comparatively, values of $k$ for oxidation of monosaccharides at different pH could not be fitted using Eq. (5) (dashed lines, Fig. 3a). It seems that other factors besides the change in the fraction of species with pH are involved in the reactivity of Fe(VI) with monosaccharides. Base catalysis of monosaccharides may be one of the factors involved where the slight increase in the reaction rate at pH >8 was observed (Fig. 3a). The tendency of the conversion of fructose to glucose in alkaline medium increases with increase in pH because such transformation is base catalyzed. Significantly, this conversion involves opening of the cyclic ring structure before fructose can be transformed to glucose. As the pH increased beyond 8.0, higher concentrations of open structures of monosaccharides are expected than those of closed (or ring) structures. Open structures of carbohydrates are more susceptible to oxidation than the ring structures. Proportions of open structures (i.e. active reductant) would increase with increase in pH and may increase the reaction rate at higher pH as observed in the present study. Increase in the formation of the active reductant form of glucose with increase in pH has also been experimentally determined (Roepke and Ort, 1931).

The disaccharide, sucrose and its chlorinated derivative, sucralose behave differentially from monosaccharides because they are non-reducing agents due to the link between C-1 and C-2 (1→2) anomeric carbons (Fig. SM-1). Rates are not expected to be influenced by an increase in the hydroxide ion concentration. Therefore their rates of oxidation are solely dependent on the predominant Fe(VI) species present at that pH. Although maltose is a reducing sugar, it behaved more like the other disaccharides, and explanation of such observed rates will stimulate further studies in this area through the investigation of oxidation rates of a multitude of other disaccharides.

**Table 1**

<table>
<thead>
<tr>
<th>Substrate (S)</th>
<th>$n$</th>
<th>$k_{10^{-1}}$ M$^{-1}$ s$^{-1}$ at pH 9.0</th>
<th>$k_{10^{-3}}$ M$^{-1}$ s$^{-1}$</th>
<th>$k_{10^{-1}}$ M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (G)</td>
<td>1.02 ± 0.07</td>
<td>1.6 ± 0.1</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fructose (F)</td>
<td>0.97 ± 0.04</td>
<td>2.1 ± 0.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Maltose (G-G)</td>
<td>0.93 ± 0.07</td>
<td>2.5 ± 0.3</td>
<td>(6.8 ± 0.3) × 10$^{-1}$</td>
<td>(2.2 ± 0.2) × 10$^{-1}$</td>
</tr>
<tr>
<td>Sucrose (G-F)</td>
<td>1.19 ± 0.07</td>
<td>1.0 ± 0.1</td>
<td>(5.3 ± 0.4) × 10$^{-1}$</td>
<td>(0.7 ± 0.1) × 10$^{-1}$</td>
</tr>
<tr>
<td>Sucralose</td>
<td>1.20 ± 0.11</td>
<td>1.3 ± 0.1</td>
<td>(5.7 ± 0.3) × 10$^{-1}$</td>
<td>(1.2 ± 0.1) × 10$^{-1}$</td>
</tr>
</tbody>
</table>
The kinetics of the oxidation of selected carbohydrates and sucralose by Fe(VI) were shown to be first-order with respect to each reactant and the observed second-order rate constants, \( k \), increased with a decrease in pH for disaccharides. However, the pH dependence for monosaccharides was different in which initial rate constant decreases were followed by increases at pH \( \geq 8.0 \), which were attributed to the hydroxide catalyzed ring opening/isomerization of fructose and glucose. Comparison of the reactivity of Fe(VI) with other oxidants suggests that free radical species such as -OH, have much higher reactivity than Fe(VI) towards carbohydrates. The reactivity of Fe(VI) with sucralose and carbohydrates may be enhanced by an Fe(VI)-TiO\(_2\)-UV system, which would likely generate the reactive species -OH and Fe(VI) to oxidize substrates more efficiently. An ozone-TiO\(_2\)-UV system may also be appropriate in degrading carbohydrates in water.

### References


