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ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES FOR REMOVAL OF TOXIC/PERSISTENT ORGANIC POLLUTANTS FROM WATER

Oxidation of artificial sweetener sucralose by advanced oxidation processes: a review

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Abstract Sucralose, a chlorinated carbohydrate, has shown its increased use as an artificial sweetener and persistently exists in wastewater treatment plant effluents and aquatic environment. This paper aims to review possible degradation of sucralose and related carbohydrates by biological, electrochemical, chemical, and advanced oxidation processes. Biodegradation of sucralose in waterworks did not occur significantly. Electrochemical oxidation of carbohydrates may be applied to seek degradation of sucralose. The kinetics of the oxidation of sucralose and the related carbohydrates by different oxidative species is compared. Free chlorine, ozone, and ferrate did not show any potential to degrade sucralose in water. Advanced oxidation processes, generating highly strong oxidizing agent hydroxyl radicals ($^{\bullet}$OH), have demonstrated effectiveness in transforming sucralose in water. The mechanism of oxidation of sucralose by $^{\bullet}$OH is briefly discussed.

Keywords Degradation · Carbohydrates · Saccharides · Sugars · Electrochemical oxidation · Ozonation · Hydroxyl radical · Ferrate

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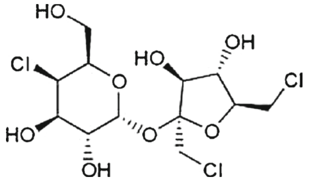
Introduction

The consumption of artificial sweeteners is increasing every year, and more than 6,000 food products contain these sweeteners (Myers 2007). Hence, the global market of artificial sweeteners is more than 500 million dollars (Bennett 2013). Among several sweeteners used in food products, sucralose (1,6-dichloro-1,6-dideoxy-β-D-fructofuranosyl-4-chloro-4-deoxy-α-D-galactopyranoside) (Table 1) (Tollefsen et al. 2012) has shown increasing trend of consumption since its commercial development. Sucralose is generally prepared by selectively substituting three hydroxyl groups of sucrose with three chlorine atoms. Sucralose is about 600 times sweeter than the parent molecule, sucrose, and this intense sweetness of sucralose resulted in its use in a wide variety of food products and pharmaceuticals. The current consumption of sucralose is ~2,000 t per year in which the USA leads the consumption by using more than ~1,500 t per year. The consumption in Europe is ~400 t per year.

Sucralose is a white crystalline powder and is almost odorless. It has high melting temperature (Table 1) (Tollefsen et al. 2012; Grotz and Munto 2009; Jenner and Smithson 1989; Lange et al. 2012) and is considered thermally stable. Sucralose has low values of vapor pressure and Henry's Law constant (Table 1). In addition, low values of air–water partitioning and octanol–water coefficient suggest high stability of sucralose in water. Half-life of sucralose in water has been suggested to be several years (Scheurer et al. 2009). Sucralose possesses hydrogen bond donor (AH)/Lewis base (B) system which provides sweet taste due to interaction between sucralose and the receptor site. In the sucralose molecule, the AH group is –OH, which is weakly acidic. The value of pK_a indicates the neutral form of sucralose that would be present at pH of the natural water (Table 1). As shown in Table 1, the molecular structure of sucralose has shortages of aromatic rings and double bonds to act as

Table 1 Structure and selected properties of sucralose [data taken from Tollefsen et al. (2012), Grotz and Munro (2009), Jenner and Smithson (1989), and Lang et al. (2012)]

Structure	
Molecular Formula	$C_{12}H_{19}Cl_3O_8$
Molecular weight (g/mol)	397.63
Sugar equivalence	600
Melting point (°C)	236.8
Vapor pressure (mm Hg)	3.25×10^{-14}
Water solubility (g/L) at 20 °C	282
Henry Law Constant atm-m^3/mol	3.99×10^{-19}
log K_{OW}/octanol-water coefficient	-0.49, -0.51, and -1.00
log K_{OW}/air-water coefficient	-16.8
log K_{OC} (soil-organic carbon coefficient)	0.7 to 1.0
pK_a	11.8

chromophores and, hence, has very low molecular extinction coefficient in the UV region (Kee and Linden 2013).

Sucralose is not easily metabolized in the human body and up to 92 % of the taken amount excretes in feces and urine (Robers et al. 2000). Under very high acidic conditions, sucralose slowly decomposes to two monosaccharides, 1,6-dichlorofructose and 4-chlorogalactose. Only less than 1 % initial sucrose was degraded after 1 year at solution pH 3 and 25 °C while no detectable hydrolysis was noticed at pH 4 and 6 (Grice and Goldsmith 2000). Since hydrolysis degradation of sucralose does not seem to be a dominating pathway and therefore no decomposition of sucralose due to hydrolysis is thus expected under conditions of natural water (Soh et al. 2011). The majority of the excreted sucralose entering sewage wastewater remains in its original form.

The biodegradation of sucralose in soil has been studied (Lapin-Scott et al. 1987; Labare and Alexander 1994; Buerge et al. 2011). In the initial work, the biological degradation of sucralose was found, but microorganism species causing the degradation were not identified (Lapin-Scott et al. 1987). In the later study, relatively high metabolism rates (35–60 %) were observed in 35 days when aerobic soil was spiked to sucralose (Labare and Alexander 1994). In a more recent work on the biodegradation of sucralose in soil, the half-lives of up to ~4 months were seen (Buerge et al. 2011). These studies suggest that sucralose is not biologically inert, but it can be biodegraded at variable rates, which depends on the bacterial assemblage that exists in the system (Mead et al. 2009). However, the results obtained in the aerobic and anaerobic biological reactors, which were fed with 1 g/L sucralose showed almost no biodegradation for 62 days (Torres et al. 2011). These slow or no biodegradation results indicate that once sucralose from different sources enters into the sewage treatment plants, it may not decompose significantly and likely transfer into the aquatic environment. Therefore, sucralose at certain concentration levels has been measured in the aquatic environment (Tollefsen et al. 2012; Scheurer et al. 2009; Kokotou et al. 2012). The concentration of sucralose has been found in the range from nanogram per liter to microgram per liter in wastewater, surface water (rivers and lake), ground waters, and drinking water of the European Union and North America (Scheurer et al. 2009; Kokotou et al. 2012; Mawhinney et al. 2011; Loos et al. 2009; Neset et al. 2010; Minten et al. 2011; Ferrer and Thurman 2010).

Currently, there are few concerns of sucralose because it is considered safe for human consumption, and the 5 mg/kg body weight per day has been set as acceptable daily intake (Grotz and Munro 2009; Brusick et al. 2010; Viberg and Fredriksson 2011). However, ecotoxicological impact assessment of sucralose is in progress. The bioaccumulation studies using different aquatic organism showed the uptake of sucralose that reached within 48 h, and the bioconcentration factors were <1.0, 1.6–2.2, and <1.0 for freshwater alga *Pseudokirchneriella subcapitata*, crustacean *Dalphnia magna*, zebrafish *Danio rerio*, respectively (Lillicrap et al. 2011). This suggests low bioaccumulation potential of sucralose in aquatic organisms. Additionally, no significant acute/chronic toxicity in aquatic organisms was observed (Lillicrap et al. 2011; Wiklund et al. 2012). A study on the impact of sucralose on the aquatic plant, *Lemna gibba*, showed no inhibition of plant cotyledon uptake (Soh et al. 2011). Wet weight, frond number, and growth rates in the plant were not affected (Soh et al. 2011).

The use of sucralose is estimated to be increasing in the coming years, and the US Environmental Protection Agency (USEPA) has flagged it as an emerging contaminant (Richardson and Ternes 2011); we therefore aimed to review the potential treatments of sucralose by chemical and advanced oxidation treatment processes. This paper first presents the electrochemical oxidation of carbohydrates in aqueous solution. This section is followed by discussion on the oxidation of sucralose by chlorine, ozone, and ferrate ($Fe^{VI}O_4^{2-}$, Fe(VI)). Finally, the potential role of advanced oxidation processes (AOP) in transforming sucralose into oxidized products (OPs) is summarized.

Electrochemical oxidation

The literature showed no study on the electrochemical oxidation of sucralose; however, several studies on the electro-oxidation of carbohydrates have been performed using different electrodes made of various metals such as copper, nickel, gold, and platinum (Parpot et al. 2006). Modified surfaces of metals and metal complexes have also been applied to oxidize glucose and some other carbohydrates (Arvinte et al. 2011). These studies have been carried out with aims of the development of amperometric sensors and analytical detection of carbohydrates (Kimmel et al. 2012). For example, a boron-doped diamond (BDD) electrode was applied for electrochemical detection of saccharides for flow injection analysis (FIA) (Hayashi et al. 2012). The oxidation of these compounds occurred at high applied potentials, and hence, the BDD electrode was suitable for performing electrochemical measurements. A separate study showed that the oxidation of aldose at low potential was possible using particular kinds of Rh porphyrins on carbon black electrode (Yamazaki et al. 2010). In this study, it was found that the onset potential to oxidize aldoses was much lower than those from the other complex-based catalysts. Significantly, an analytical analysis of the products demonstrated that the reaction likely occurred through the involvement of two-electron oxidation of the aldehyde group. In other works, saccharides were oxidized using carbon nanotube (CNT)-NiCo-oxide composites in alkaline solutions in order to develop a new sensor for an amplified electrochemical detection (Arvinte et al. 2011). In recent years, the emphasis was made to carry out electro-oxidation of saccharides at low potential for fuel cells (Yamazaki et al. 2010).

A few studies on the oxidation of carbohydrates using metallic electrodes have been carried out to selectively oxidize the alcohol group and to understand the steps of the mechanism (Parpot et al. 2006, 2010; Barbier et al. 2006; Das et al. 2007). A use of the catalytic amount of 2,2,6,6-tetramethyl-1-piperidinyl-oxy (TEMPO) as redox mediator in the oxidation of carbohydrates using glassy carbon anode at controlled potential 0.5 V vs. AgCl/Ag in alkaline medium gave selective oxidation of primary alcohol, without free aldehyde, to the corresponding sodium urinate that had high faradaic yields. However, selectivity to uronic acid decreased when free aldehyde or hemiacetal groups were present (Parpot et al. 2010). Other by-products were formed in the presence of free aldehyde (Parpot et al. 2010). The relationship between electro-activity and structure of monosaccharides was developed by studying the electrochemical behavior at a gold electrode in alkaline medium (Parpot et al. 2006). The oxidation of the aldehyde hydrate (or hemiacetal) at C1 carbon atom, primary alcohol, and vicinal diols occurred at $E<0.7$ V vs. NHE, 0.8–1.1 V vs. RHE, and 1.1–1.3 V vs. NHE, respectively (Parpot et al. 2006). Reaction pathways for different functional groups are presented in Fig. 1 (Parpot et al. 2006). In the oxidation of aldehyde, the initial step was adsorption, followed by subsequent oxidation of the aldehyde hydrate (and/or hemiacetal) at potential between 0.4 and 0.8 V vs. NHE (Fig. 1a). The formation of galactonic acid, galactaric acid, and galacturonic acid as main products suggested the oxidation of primary alcohol (Fig. 1b). Figure 1c shows the cleavage of C–C bonds in the potential range between 1.1 and 1.3 V vs. NHE in the vicinal diols oxidation. In this case, the spatial orientation of –OH groups had very significant role.

A study of the oxidation of carbohydrates has also been carried out in 0.1 M NaOH using the modified gold crystal surface (111) prepared under potential deposition (Aoun et al. 2003). A number of metals and catalytic effects were examined in this study. The glucose oxidation occurred at −0.44 V (vs. Ag/AgCl). The catalytic activity was much better for Ag adatoms on Au electrodes than those for Cu, Co, Ru, Cd, Ir, and Pt. A significant oxidation peak was obtained for aldose kind monosaccharides and disaccharides (glucose, xylose, mannose, maltose, and lactose). However, a disaccharide, sucrose, did not have any oxidation peak. Interestingly, no oxidation current was observed for gluconolactone and mannolactone at negative potentials at which oxidation of glucose took place. This suggests that no more than two-electron oxidation steps occurred.

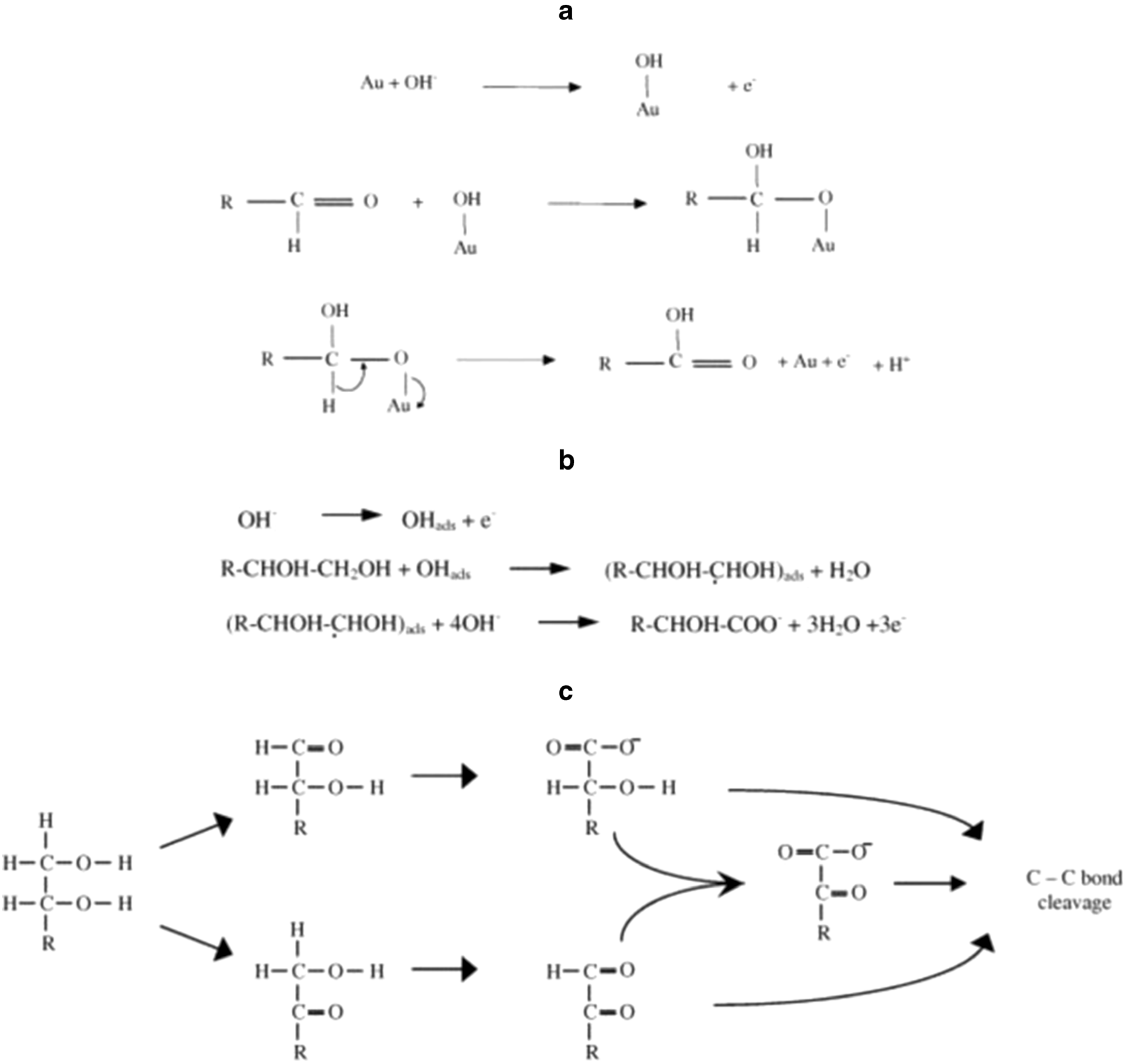


Fig. 1 **a** Reaction pathway in the oxidation of the aldehyde on a gold electrode, **b** reaction pathway in the oxidation of primary alcohol on a gold electrode reaction pathway in the oxidation of primary alcohol on a gold electrode, and **c** reaction pathway in the oxidation of vicinal diols on a gold electrode (adapted from (Parpot et al. 2006) with the permission of Elsevier Inc.)

Chlorination

There are few studies on the decomposition of sucralose using chlorine (Soh et al. 2011; Torres et al. 2011; Scheurer et al. 2010). No reaction between 1 and 25 μM chlorine was seen for 5 h (Soh et al. 2011). In laboratory batch tests using 1 μg/l sucralose in drinking water at pH 7, free chlorine at dosages of 0.2 and 1 mg/l were added (Scheurer et al. 2010). Sucralose did not transform in batch tests. In other works, experiments were conducted using free chlorine over a wider concentration range of 0.1–100 mM free chlorine (Torres et al. 2011). The initial concentration of sucralose was 1.0 mM. After 96 h of contact time, only 1.5 % (15 μM) of sucralose degraded using 0.1-mM free chlorine. The decomposition increased to 79 % in the case of using 100-mM free chlorine. A usual concentration of free chlorine in the wastewater treatment plants (WWTPs) is 0.1 mM and the contact time is <10 min; therefore, chlorination would not degrade sucralose in WWTPs. These experiments allowed estimating the second-order rate constant between chlorine and sucralose as $1.6 \pm 0.9 \times 10^{-3}\ M^{-1}\ s^{-1}$ (Table 2).

Table 2 Rate constants of sucralose and related carbohydrates with different oxidants at 25 °C

Oxidant	pH	Glucose k, M^{-1} s^{-1}	pH	Maltose k, M^{-1} s^{-1}	pH	Sucrose k, M^{-1} s^{-1}	pH	Sucralose k, M^{-1} s^{-1}
Chlorine	–	–	–	–	–	–	7.0	1.6×10^{-3}[d]
ClO_2	–	$<1.0\times10^{-2}$[a]	–	–	–	–	–	–
O_3	6.0	4.8×10^{0}[b]	6.0	6.9×10^{0}[b]	5.5	2.3×10^{0}[b]	–	–
$^{\bullet}OH$	7.5	1.5×10^{9}[b]	6.5	2.3×10^{9}[b]	7.0	2.3×10^{9}[b]	7.4	1.5×10^{9}[e]
$SO_4^{\bullet-}$	–	–	–	–	–	–	7.4	1.7×10^{8}[e]
$CO_3^{\bullet-}$	9.3	4.3×10^{5}[c]	–	–	8.3	2.4×10^{4}[c]	–	–
Fe(VI)	7.0	2.0×10^{-1}	7.0	5.0×10^{-1}	7.0	3.7×10^{-1}	7.0	4.0×10^{-1}

[a] From (Hoigne and Bader 1994)

[b] From (National Institute of Science and Technology and Web 2013)

[c] From (Stenman et al. 2003)

[d] From (Torres et al. 2011)

[e] From (Toth et al. 2012)

Carbohydrates are constituents of organic matter and biomolecules present in water (Hung et al. 2001; Sigleo 1996). A work on the chlorination of carbohydrates has been carried out to learn role of such reactions in the formation of trihalomethanes (THMs) (Navalon et al. 2008). Carbohydrates resulted in significant concentrations of THMs (100 ppb) upon chlorination at a dose of 10 ppm of water containing 2 ppm dissolved organic carbon (DOC) at pH 8.0. The change in pH from acidic to basic range had great influence on the formation of THMs. Acidic pH values did not cause the formation of THMs while slight increase in THMs was observed at basic pH. The presence of both chloride and bromide ion in water increased the formation of THMs. Bromide was more efficient than that of chloride to cause the formation of THMs. Overall, carbohydrates present in wastewater influent may contribute to the formation of THMs in disinfection using chlorine.

Advanced oxidation processes

Ozonation and hydroxyl radical

In the last few years, studies have been performed to see the effectiveness of ozone to degrade sucralose in water (Soh et al. 2011; Torres et al. 2011; Scheurer et al. 2010; Hollender et al. 2009). In batch tests, oxidation of 1 μg/l sucrose was sought in water containing 0.9 mg/l DOC and 5 mM HCO_3^- at pH 7.3 (Scheurer et al. 2010). Four different dosages of ozone (0.5, 1.0, 2.0, and 5.0 mg/l) were tested, and samples were subjected to determine sucralose concentration at 1 and 60-min contact time. This study also performed field experiments using ozone. The transformation of sucralose was less than 20 % in laboratory and field experiments. The results showed that sucralose would likely be present in waterworks (Scheurer et al. 2010). Other study also showed similar results in which 96-h contact time between sucralose and ozone was established (Torres et al. 2011). Persistence of sucralose in ozone treatment is also supported by another work, which showed only 31 % sucralose likely to be removed in a water treatment plant upgraded with ozonation (Hollender et al. 2009).

A detailed study on ozonation of sucralose and other sweeteners has recently been performed (Soh et al. 2011). The results for the degradation of 1-μM artificial sweeteners after a 1-h treatment with 100-μM ozone are presented in Fig. 2a (Soh et al. 2011). The residual concentration of sucralose was 6 % after 1 h. Comparatively, other sweeteners, acesulfame-K and caffeine, were below detection levels after only 5 min. Ozone may oxidize compounds through direct reaction with ozone and also via radical-mediated oxidation. Sucralose does not appear to have direct site(s) of attack by molecular ozone; the oxidation of sucralose was hypothesized to be due to the hydroxyl radical ($^{\bullet}OH$) generated in the oxidative system. This hypothesis was tested by adding 0.5 mM t-butanol as a radical quencher. As shown in Fig. 2b, retardation in degradation of sucralose was observed. Also, degradations of acesulfame-K and caffeine were slower when no quencher was present (Fig. 2b). These results indicate that the breakdown of sucralose and other sweeteners was through radical pathways. However, organic matter present in treatment of water may decrease the efficiency by successfully competing for the $^{\bullet}OH$ and may decrease the efficiency of the degradation of artificial sweeteners (Soh et al. 2011).

In a more recent study, kinetic measurements on the reactivity of artificial sweeteners including sucralose were conducted using pulse radiolysis technique (Toth et al. 2012). The

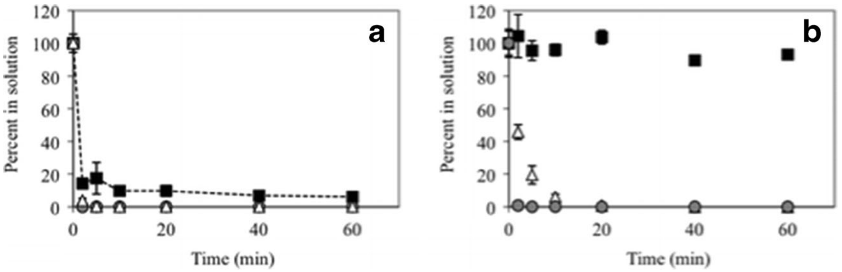


Fig. 2 Results of ozonation for (*black square*) sucralose, (*gray circle*) caffeine, (*white triangle*) acesulfame-K. **a** Decreasing amount of contaminant after 1 h of exposure to 100 μM ozone to 1 μM of contaminant (initial first order reaction rates, 0.00427 s^{-1}, 0.0209 s^{-1} for sucralose and acesulfame-K, respectively, caffeine was immeasurable). **b** Results when t-butanol, a hydroxyl radical quench is added to the ozone and contaminant (first order reaction rates, 0.0129 s^{-1}, 0.0398 s^{-1} for acesulfame-K and caffeine, respectively). Sucralose did not degrade in the presence of t-butanol indicating that sucralose degradation by ozone is through radical-mediated reactions. *Error bars* represent 95 % confidence interval (n=3) (reproduced from (Soh et al. 2011) with the permission of the American Chemical Society)

second-order rate constant for the reaction of sucralose with $^{\bullet}OH$ (Eq. (1)) was determined of the order of 10^9 M^{-1} s^{-1} (Eq. 1, Table 2). Other sweeteners, acesulfame K, aspartame, rebaudioside A, and saccharin, had rate constants of 3.80×10^9, 6.06×10^9, 9.97×10^9, and 1.85×10^9 M^{-1} s^{-1}, respectively (Toth et al. 2012).

$$\text{Sucralose} + {}^{\bullet}\text{OH} \rightarrow \text{Products} \qquad k_1 = 1.50 \times 10^9 \text{M}^{-1}\text{s}^{-1} \quad (1)$$

The values of the rate constants for the reactivity of artificial sweeteners with $^{\bullet}OH$ support the decomposition of sweeteners during ozonation that occurred through radicals generated in the system.

The degradation efficiency of $^{\bullet}OH$ for sweeteners has also been calculated, and the values are presented in Fig. 3 (Toth et al. 2012). Details of the calculation can be found in this study (Toth et al. 2012). Sucralose had the highest degradation efficiency of 98 % (Fig. 3). Degradation efficiencies for other sweeteners were in range from 53 to 68 %. It should be pointed out that these degradation efficiencies may decrease in the presence of inorganic (e.g., HCO_3^-) and organic (e.g., natural organic matter, NOM) constituents of the wastewater, which can compete for $^{\bullet}OH$ radicals (Eqs. 2 and 3).

$$\text{HCO}_3^- + {}^{\bullet}\text{OH} \rightarrow \text{Products} \qquad k_2 = 8.5 \times 10^6 \text{M}^{-1}\text{s}^{-1} \quad (2)$$

$$\text{NOM} + {}^{\bullet}\text{OH} \rightarrow \text{Products} \qquad k_3 = 2.25 \times 10^8 \text{M}^{-1}\text{s}^{-1} \quad (3)$$

The concentration of these likely constituents in wastewater may be much higher than those of sweeteners, and therefore, the degradation efficiencies of $^{\bullet}OH$ for sweeteners may decrease.

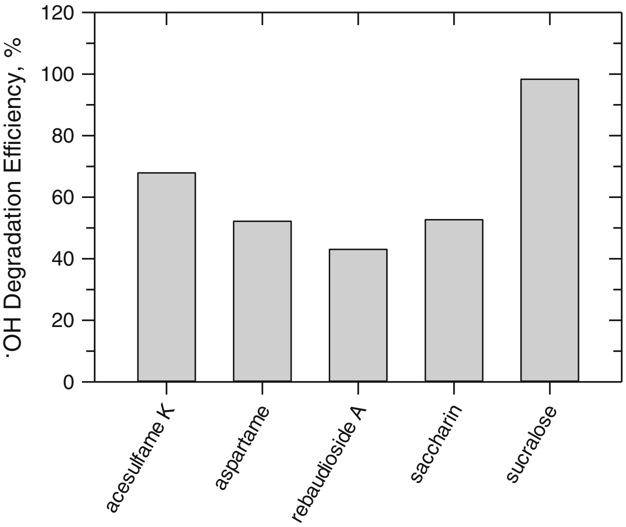


Fig. 3 Hydroxyl radical degradation efficiencies for sweeteners (data were taken from (Toth et al. 2012))

UV/H_2O_2 photooxidation

Degradation of sucralose has also been sought using ultraviolet (UV) light (Grotz and Munto 2009; Soh et al. 2011; Torres et al. 2011). In a photochemical reactor, sucralose did not degrade after 5 h UV exposure (Soh et al. 2011). Sucralose also did not decrease significantly when UV light irradiation lasted for 24 h (Torres et al. 2011). This is not surprising because sucralose has low molar extinction coefficient in the UV region (Grotz and Munto 2009). The addition of NOM as a photosensitizer did not result in any additional degradation of sucralose (Soh et al. 2011). The photolysis of sucralose was therefore carried out in the presence of H_2O_2 to make use of $^{\bullet}OH$ radicals to degrade sucralose (Grotz and Munto 2009). A 1-kW medium pressure mercury vapor lamp emitting polychromatic spectrum at $\lambda > 200$ nm was applied. A photochemical effect may come from the overlap of absorbance spectra of lamp and sucralose. The degradation of sucralose occurred in the UV/H_2O_2 system. The role of radicals was demonstrated by monitoring the decay of sucralose in the presence and absence of a radical quencher, methanol. In the absence of a quencher, the degradation of sucralose was efficient.

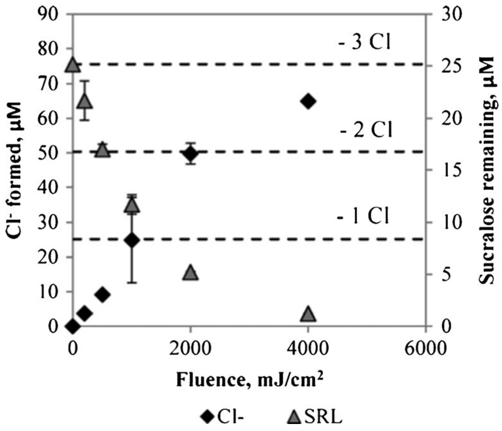


Fig. 4 Decay of sucralose during UV/H_2O_2 treatment using a medium pressure Hg vapor UV lamp and subsequent increase in chloride ion with increasing fluence (reproduced from (Grotz and Munto 2009) with the permission of the American Chemical Society)

The mechanism of the degradation of sucralose in the UV/H_2O_2 was examined by determining the concentration of Cl^- and identifying transformation products (Soh et al. 2011). Figure 4 shows the formation of Cl^- as the concentration of sucralose decreased. In Fig. 4, the dashed lines correspond to the formation of 1, 2, and 3 mol of Cl^- for every mole of sucralose. The data point above the dashed line at 4,000 mJ/cm^2 fluency suggests that some of the sucralose lost all three chlorines. Furthermore, 1 chlorine mol was formed even at an incomplete decomposition of sucralose. The transformation products of sucralose were separated and then identified using ion trap mass spectrometry. The proposed pathways are shown in Fig. 5. The chlorine on the cyclic moiety is the weakest C–Cl bond of sucralose, and therefore, suggested pathways involved the initial degradation of sucralose through substitution of a single chlorine by a hydroxyl group. The cyclic moiety could be the preferential site for this initial step. Further hydroxyl group substitutions were suggested, which ultimately resulted in full dechlorination of sucralose. Significantly, sucrose does not seem to be the final oxidized product of sucralose because the initial step also broke the six-member ring (Fig. 5). Finally, transform products include sugar alcohol and fructose.

Ferrate

In the past decade, ferrate(VI), FeO_4^{2-}, commonly called ferrate, has become an emerging chemical for disinfection, oxidation, and coagulation, and several researchers have explored its applications in treating a wide range of microorganisms, micropollutants, toxic metals, and nutrients (Jiang et al. 2005, 2006, 2009, 2012, 2013; Jiang and Zhou 2013; Jiang 2007; Lee and von Gunten 2010; Lee et al. 2008, 2009; Casbeer et al. 2013; Prucek et al. 2013; Sharma et al. 2008, 2013; Anquandah et al. 2011, 2013; Sharma 2013). Based on such novel applications of ferrate, the kinetics of the oxidation of sucralose and related carbohydrates (glucose, fructose, maltose, and sucrose) have been studied as a function of pH at 25 °C (Sharma et al. 2012). The second-order rate constants are given in Table 2. Both sucrose and sucralose had lower reactivity than that of other studied carbohydrates. The values of the rate constant indicate

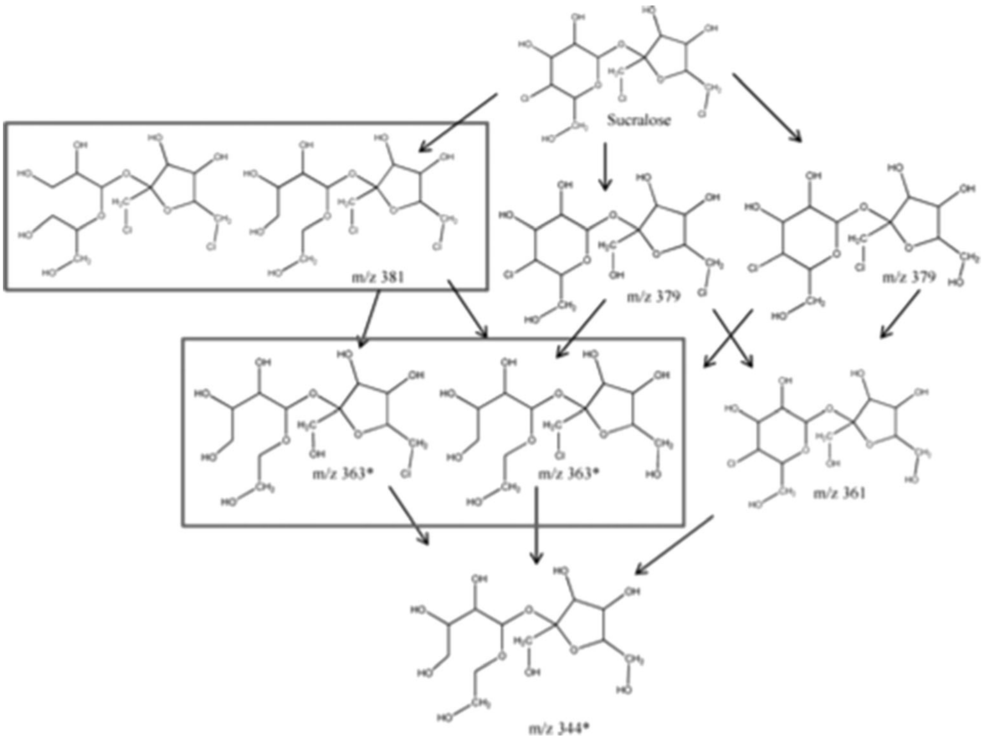


Fig. 5 Proposed products and degradation pathway of sucralose during UV/H_2O_2 photolysis (Products marked with were not detectable. The preferential pathway for degradation is emphasized with *boxes*) (reproduced from (Grotz and Munto 2009) with the permission of the American Chemical Society)

that ferrate may not be feasible to degrade sucralose in water, similar to chlorination and ozonation.

The comparison of the reactivity of sucralose by different oxidant species in conventional and advanced oxidation processes can be seen in Table 2 (Torres et al. 2011; Toth et al. 2012; Hoigne and Bader 1994; National Institute of Science and Technology and Web 2013; Stenman et al. 2003). The order of the reactivity with sucralose is $SO_4^{\cdot-} \approx {}^{\bullet}OH >$ ferrate > free chlorine. Both radical species react several orders of magnitude faster than the free chlorine or ferrate. It seems that both free chlorine and ferrate do not find sufficient electron-rich moiety in the reductant to cause oxidative transformation of sucralose. This sluggish reactivity of chemical oxidants with sucralose suggests that these oxidants may not be suitable for degrading sucralose in water. It seems that oxidative species of advance oxidation processes would effectively degrade sucralose in water.

Conclusions

There has been increasing research on sucralose towards understanding its effect on human health and the environment. Sucralose persists in the aquatic environment for a long period of time, and it has been found in the water cycle. Various treatment processes attempted to degrade sucralose in waterworks. Chlorine and molecular ozone as well as ferrate did not appear to be effective in oxidizing sucralose in water. UV photolysis was also not effective in photooxidizing sucralose. Contrariwise, the strong oxidizing agent ${}^{\bullet}OH$ reacted with sucralose at a second-order rate constant of $10^9\ M^{-1}\ s^{-1}$, and therefore, the ${}^{\bullet}OH$, generated in the decomposition of ozone in water and in the UV/H_2O_2, showed great potential to transform sucralose in water. The mechanism involved hydroxyl substitution of the chlorine atoms on the sucralose to transform it into environmentally benign fructose and sugar alcohol. The ${}^{\bullet}OH$ can be generated through homogeneous and heterogeneous Fenton reactions, photo-Fenton reactions, anodic oxidation using high O_2- over voltage anodes, and electro-Fenton process, and future studies may include to see the effectiveness of these advanced oxidation processes to degrade sucralose in water.

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References

Anquandah GAK, Sharma VK, Knight DA, Batchu SR, Gardinali PR (2011) Oxidation of trimethoprim by ferrate(VI): kinetics, products, and antibacterial activity. Environ Sci Technol 45:10575–10581

Anquandah GAK, Sharma VK, Panditi VR, Gardinali PR, Kim H, Oturan MA (2013) Ferrate(VI) oxidation of propranolol: kinetics and products. Chemosphere 91:105–109

Aoun S, Bang GS, Koga T, Nonaka Y, Sotomura T, Taniguchi I (2003) Electrocatalytic oxidation of sugars on silver-UPD single crystal gold electrodes in alkaline solutions. Electrochem Commun 5:317–320

Arvinte A, Sesay A, Virtanen V (2011) Carbohydrates electrocatalytic oxidation using CNT-NiCo-oxide modified electrodes. Talanta 84:180–186

Barbier M, Breton T, Servat K, Grand E, Kokoh B, Kovensky J (2006) Selective TEMPO-catalyzed chemicals vs. electrochemical oxidation of carbohydrate derivatives. J Carbohydr Chem 25:253–266

Bennett D (2013) The intense sweetener world, Ehrenberg center for research in marketing. (http://www.lsbu.ac.uk/bus-ehrenberg/documents/High%20Intensity%20Sweeteners.pdf. Accessed on 28 May 2013

Brusick D, Grotz VL, Slesinski R, Kruger CL, Hayes AW (2010) The absence of genotoxicity of sucralose. Food Chem Toxicol 48:3067–3072

Buerge IJ, Keller M, Buser H-R, Müller MD, Poiger T (2011) Saccharin and other artificial sweeteners in soils: estimated inputs from agriculture and households, degradation, and leaching to groundwater. Environ Sci Technol 45:615–621

Casbeer EM, Sharma VK, Zajickova Z, Dionysiou DD (2013) Kinetics and mechanism of oxidation of tryptophan by ferrate(VI). Environ Sci Technol 47:4572–4580

Das D, Sen PK, Das K (2007) Carbohydrate electro-oxidation on chemically prepared MnO_2. J Electroanal Chem 611:19–25

Ferrer I, Thurman EM (2010) Analysis of sucralose and other sweeteners in water and beverage samples by liquid chromatography/time-of-flight mass spectrometry. J Chromatogr A 1217:4127–4134

Grice HC, Goldsmith LA (2000) Sucralose—an overview of the toxicity data. Food Chem Toxicol 38:S1–S36

Grotz VL, Munro IC (2009) An overview of the safety of sucralose. Regul Toxicol Pharmacol 55:1–5

Hayashi T, Sakurada I, Honda K, Motohashi S, Uchikura K (2012) Electrochemical detection of sugar-related compounds using boron-doped diamond electrodes. Anal Sci 28:127–134

Hoigne J, Bader H (1994) Kinetics of reactions of chlorine dioxide (OClO) in water—I. Rate constants for inorganic and organic compounds. Water Res 28:45–55

Hollender J, Zimmermann SG, Koepke S, Krauss M, Mcardell CS, Ort C, Singer H, Von Gunten U, Siegrist H (2009) Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration. Environ Sci Technol 43:7862–7869

Hung C-C, Tang D, Warnken KW, Santschi PH (2001) Distributions of carbohydrates, including uronic acids, in estuarine waters of Galveston Bay. Mar Chem 73:305–318

Jenner M, Smithson A (1989) Physicochemical properties of the sweetener sucralose. J Food Sci 54:1646–1649

Jiang JQ (2007) Research progress in the use of ferrate(VI) for the environmental remediation. J Hazard Mater 146:617–623

Jiang JQ, Zhou Z (2013) Removal of pharmaceutical residues by ferrate(VI). PLoS ONE 8:e55729

Jiang JQ, Yin Q, Zhou JL, Pearce P (2005) Occurrence and treatment trials of endocrine disrupting chemicals (EDCs) in wastewaters. Chemosphere 61:544–550

Jiang JQ, Wang S, Panagoulopoulos A (2006) The exploration of potassium ferrate(VI) as a disinfectant/coagulant in water and wastewater treatment. Chemosphere 63:212–219

Jiang JQ, Stanford C, Alsheyab M (2009) The online generation and application of ferrate(VI) for sewage treatment-a pilot scale trial. Sep Purif Technol 68:227–231

Jiang JQ, Zhou Z, Pahl O (2012) Preliminary study of ciprofloxacin (cip) removal by potassium ferrate(VI). Sep Purif Technol 88:95–98

Jiang JQ, Zhou Z, Patibandla S, Shu X (2013) Pharmaceutical removal from wastewater by ferrate(VI) and preliminary effluent toxicity assessments by the zebrafish embryo model. Microchem J 110:239–245

Kee OS, Linden KG (2013) Re-engineering an artificial sweeteners: transforming sucralose residuals in water via advanced oxidation. Environ Sci Technol 47:6799–6805

Kimmel WK, LeBlanc G, Meschievitz ME, Cliffel DE (2012) Electrochemical sensor and biosensors. Anal Chem 84:685–707

Kokotou MG, Asimakopoulos AG, Thomaidis NS (2012) Artificial sweeteners as emerging pollutants in the environment: analytical methodologies and environmental impact. Anal Methods 4:3057–3070

Labare MP, Alexander M (1994) Microbial cometabolism of sucralose, a chlorinated disaccharide, in environmental samples. Appl Microbiol Biotechnol 42:173–178

Lange FT, Scheurer M, Brauch H-J (2012) Artificial sweeteners—a recently recognized class of emerging environmental contaminants: a review. Anal Bioanal Chem 403:2503–2518

Lapin-Scott HM, Holt G, Bull AT (1987) Microbial transformation of 1, 6-dichloro-1,6-dideoxy-β, D-fructofuranosyl-4-chloro-4-deoxy-α, D-galactopyranoside (TGS) by soil populations. J Appl Microbiol 3:95–102

Lee Y, von Gunten U (2010) Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). Water Res 44:555–566

Lee Y, Escher BI, von Gunten U (2008) Efficient removal of estrogenic activity during oxidative treatment of waters containing steroid estrogens. Environ Sci Technol 42:6333–6339

Lee Y, Zimmermann SG, Kieu AT, von Gunten U (2009) Ferrate (Fe(VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal. Environ Sci Technol 43:3831–3838

Lillicrap A, Langford K, Tollefsen KE (2011) Bioconcentration of the intense sweetener sucralose in a multitrophic battery of aquatic organisms. Environ Toxicol Chem 30:673–681

Loos R, Gawlik BM, Boettcher K, Locoro G, Contini S, Bidoglio G (2009) Sucralose screening in European surface waters using a solid-phase extraction-liquid chromatography-triple quadrupole mass spectrometry method. J Chromatogr A 1216:1126–1131

Mawhinney DB, Young RB, Vanderford BJ, Borch T, Snyder SA (2011) Artificial sweetener sucralose in U.S. drinking water systems. Environ Sci Technol 45:8716–8722

Mead RN, Morgan JB, Avery GB Jr, Kieber RJ, Kirk AM, Skrabal SA, Willey JD (2009) Occurrence of the artificial sweetener sucralose in coastal and marine waters of the United States. Mar Chem 116:13–17

Minten J, Adolfsson-Erici M, Björlenius B, Alsberg T (2011) A method for the analysis of sucralose with electrospray LC/MS in recipient waters and in sewage effluent subjected to tertiary treatment technologies. Int J Environ Anal Chem 91:357–366

Myers RL (2007) The 100 most important chemical compounds: a reference guide. Greenwood Publishing Group, Westport

NIST Chemical Kinetics Database. Standard Reference Database 17, Version 7.0 (Web Version), Release1.6.7 Data Version 03.2013

Navalon S, Alvaro M, Garcia H (2008) Carbohydrates as trihalomethanes precursors. Influence of pH and the presence of Cl^- and Br^- on trihalomethane formation potential. Water Res 42:3990–4000

Neset TSS, Singer H, Longrée P, Bader H-P, Scheidegger R, Wittmer A, Andersson JCM (2010) Understanding consumption-related sucralose emissions—a conceptual approach combining substance-flow analysis with sampling analysis. Sci Total Environ 408:3261–3269

Parpot P, Nunes N, Bettencourt AP (2006) Electrocatalytic oxidation of monosaccharides on gold electrode in alkaline medium: structure-reactivity relationship. J Electroanal Chem 596:65–73

Parpot P, Servat K, Bettencourt AP, Huser H, Kokoh KB (2010) TEMPO mediated oxidation of carbohydrates using electrochemical methods. Cellulose 17:815–824

Prucek R, Tuček, Kolařík J, Filip J, Marušák Z, Sharma VK, Zbořil R (2013) Ferrate(VI)-induced arsenite and arsenate removal by in situ structural incorporation into magnetic iron(III) oxide nanoparticles. Environ Sci Technol 47:3283–3292

Richardson SD, Ternes TA (2011) Water analysis: emerging contaminants and current issues. Anal Chem 83:4616–4648

Robers A, Renwick AG, Sims J, Snodin DJ (2000) The metabolic fate of sucralose in rats. Food Chem Toxicol 38(Suppl 2):S31–S41

Scheurer M, Brauch H-J, Lange FT (2009) Analysis and occurrence of seven sweeteners in German wastewater and surface water and in soil treatment (SAT). Anal Bioanal Chem 394:1585–1594

Scheurer M, Storck R, Brauch H-J, Lange FT (2010) Performance of conventional multi-barrier drinking water treatment plants for the removal of four artificial sweeteners. Water Res 44:3573–3584

Sharma VK (2013) Ferrate(VI) and ferrate(V) oxidation of organic compounds: kinetics and mechanism. Coord Chem Rev 257:495–510

Sharma VK, Li XZ, Graham N, Doong RA (2008) Ferrate(VI) oxidation of endocrine disruptors and antimicrobials in water. J Water Supply Res Technol AQUA 57:419–426

Sharma VK, Sohn M, Anquandah GAK, Nesnas N (2012) Kinetics of the oxidation of sucralose and related carbohydrates by ferrate(VI). Chemosphere 87:644–648

Sharma VK, Liu F, Tolan S, Sohn M, Kim H, Oturan MA (2013) Oxidation of β-lactam antibiotics by ferrate(VI). Chem Eng J 221: 446–451

Sigleo AC (1996) Biochemical components in suspended particles and colloids: carbohydrates in the Potomac and Patuxent estuaries. Org Geochem 24:83–93

Soh L, Connors KA, Brooks BW, Zimmerman J (2011) Fate of sucralose through environmental and water treatment processes and impact on plant indicator species. Environ Sci Technol 45:1363–1369

Stenman D, Carlsson M, Jonsson M, Reitberger T (2003) Reactivity of the carbonate radical anion towards carbohydrate and lignin model compounds. J Wood Chem Technol 23:47–69

Tollefsen KE, Nizzetto L, Huggett DB (2012) Presence, fate and effects of the intense sweetener sucralose in the aquatic environment. Sci Total Environ 438:510–516

Torres CI, Ramakrishna S, Chiu C-A, Nelson KG, Westerhoff P, Krajmalnik-Brown R (2011) Fate of sucralose during wastewater treatment. Environ Eng Sci 28:325–331

Toth JE, Rickman KA, Venter AR, Kiddle JJ, Mezyk SP (2012) Reaction kinetics and efficiencies for the hydroxyl and sulfate radical based oxidation of artificial sweeteners in water. J Phys Chem A 116: 9819–9824

Viberg H, Fredriksson A (2011) Neonatal exposure to sucralose does not alter biochemical markers of neuronal development or adult behavior. Nutrition 27:81–85

Wiklund AKE, Breitholtz M, Bengtsson B-E, Adolfsson-Erici M (2012) Sucralose—an ecotoxicological challenger? Chemosphere 86:50–55

Yamazaki S, Fujiwara N, Takeda S, Yasuda (2010) Electrochemical oxidation of sugars at moderate potentials catalyzed by Rh porphyrins. Chem Commun 46:3607–3609