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Ozone Degradation of Cellulose Model Compounds

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This paper describes kinetic studies on, and the identification of products from, the ozonolysis in aqueous solution of the cellulose model compounds methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, and anhydrocellobiitol. The purpose of these studies was to understand more clearly the processes involved in the degradation of pulp carbohydrates by ozone, a potential but little used pulp bleaching agent.

The kinetics of the ozonolysis showed that the β-glucoside reacted 1.8 times as fast as the a-glucoside under the same conditions. The rate was dependent on initial concentration of substrate showing the importance of the diffusion rate of ozone in water.

Product analysis showed that anhydrocellobiitol on ozonolysis yielded gluconolactone, glucose and anhydroglucitol as primary products, indicating that ozonolysis caused both oxidative and hydrolytic cleavage of the glycosidic bond.

These results clearly demonstrate how very susceptible pulp carbohydrates are to oxidative and hydrolytic degradation by ozone, the β-1:4 linked glucosides being much more susceptible to cleavage than the α-1:4 linked glucoside.

INTRODUCTION

The effluents from the chlorine-based bleaching sequences which are widely used in the pulp industry have been the main cause of aquatic pollution from chemical pulp mills, because it is hard to recycle these effluents in pulping processes. Oxygen-based bleaching agents generate effluent which can be recycled and thus produce no pollution problems. Oxygen, peroxide, and ozone have been studied as bleaching agents for two decades and the first two reagents are now being used commercially. However, ozone bleaching is still in its developmental stage and is far from being commercially viable.

The advantages of ozone bleaching are that it can be done at atmospheric pressure and room temperature for relatively short periods of time but it has demerits since serious depolymerization of pulp polysaccharides occurs during the bleaching (Kamishima *et al., 1976* ; Soteland, 1978 ; Mbachu and Manley, 1981a). In other words ozone would be a very valuable bleaching agent for chemical pulps if the attack on the carbohydrate fraction could be retarded.

Considerable efforts to control the carbohydrate degradation have been made by searching for protectors (Kamishima *et al.*, 1977, 1982 ; Mbachu and Manley, 1981b), by adapting multistage ozone treatment (Kobayashi et al., 1976), or by combination with the other oxygen-based bleaching methods (Soteland 1978 ; Allison 1982). However so far these methods have not been very successful. Over all, the literature data suggest that lignin in pulp is the best carbohydrate protector, and therefore use of ozone is well

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suited to the delignification and bleaching of high yield pulps as was shown by Allison (1979, 1980).

Many studies on the reaction of lignin with ozone have shown that cleavage between C-3 and C-4 positions in the guaiacyl unit is the main lignin degradation reaction (Kaneko et al., 1983 and references cited therein). However, less is known about the reaction mechanism of the depolymerization of wood polysaccharides.

Katai and Schuerch (1966) claimed that ozone attack on cellulose substances appeared to involve two mechanisms; one a free-radical chain mechanism and the other the ozone-catalyzed hydrolysis of glycosidic linkages. Deslongchamps et al. (1974) found that the acetates of methyl β-D-glucopyranosides were smoothly converted into their corresponding 5-hydroxy aldonic acid methyl esters by ozone treatment in an organic solvent whereas the acetates of methyl α-D-glucopyranosides were recovered unchanged. Recently kinetic studies by Pan *et al.* (1981) showed that methyl β-D-glucoside reacted with ozone in aqueous media nearly twice as fast as the α-anomer and also that β-anomer was attacked at the C-H bond of the C-l carbon yielding mainly gluconolactone.

This paper examines the reaction kinetics and the products obtained from the ozonolysis of the cellulose model compounds, methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, and anhydrocellobiitol. A major objective of the studies was to determine if the action of ozone caused both hydrolysis and oxidation of the carbohydrate model compounds, as was suggested by the study of Katai and Schuerch (1966). A secondary object was to determine the relative ozonolysis rates of the α- and β-1 : 4 glucosidic linkages.

MATERIALS AND METHODS

Materials

Methyl α-D-glucopyranoside (BDH) and methyl β-D-glucopyranoside (Sigma) were purchased commercially. Anhydrocellobiitol was supplied by Professor R. J. Ferrier, Victoria University of Wellington. These were used as substrates for ozonolysis without further purification.

Ozonolysis and products analysis

Ozone was generated with an OREC Model O3B1-0 Ozonator. The analysis of ozone-containing oxygen was performed by iodometric titration.

A diagram of the ozonolysis equipment is shown in Fig. 1. The substrate (one of the glucosides) was weighed into a reaction flask, dissolved in 20-30 ml of deionized and distilled water, and reacted with ozone at 25°C with a stream of oxygen containing about 2.5% ozone which passed through a fine-sintered glass bulb at a flow rate from 220 to 350 ml/min for 2-6 h.

At the desired reaction time the ozone flow was changed to a bypass and 1.0 ml of the reaction mixture was withdrawn. The amount of the starting material unchanged was analyzed by HPLC after addition of a known amount of inositol as an internal standard.

The HPLC apparatus used was a Waters Model 510 pump in combination with a Waters R401 detector. The HPLC columns used were Sugar Pak 1 eluted with water

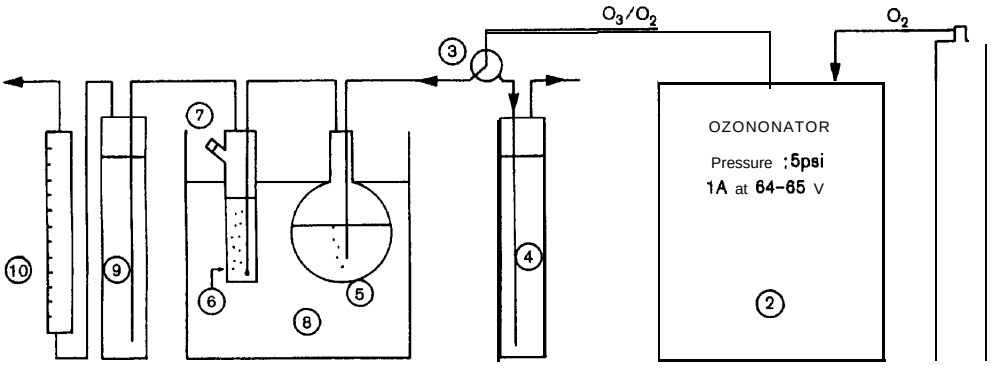

Fig. 1. Ozonolysis equipment.

at 0.6 ml/min at 90°C, that used for qualitative analysis of components being Organic Acid Column (Biorad HPX87H) eluted with 0.15% v/v H_3PO_4 solution at 0.6 ml/min at 45°C.

Identification of reaction products was carried out mainly by injecting the reaction mixture on to the HPLC and comparing their retention times with authentic standards. Gas chromatography-mass spectrometry (GC-MS) of the freeze-dried and silylated reaction products was also used for product indentification as described before (Sakai and Uprichard, 1988). Retention time (rt) and mass spectra of the products from ozonolysis of anhydrocellobiitol were as follows (all as trimethylsilyl derivatives) :

Arabinose : (rt 6.18 and 6.68 min).

Arabinolactone : (rt 6.30 min); M/Z 73 (100%), 117 (31.5), 147 (22.7), 217 (16.0), 231 (15.5), 349 (5.1, M^+-15), 364 (10.4, M^+).

1,5-Anhydroglucitol: (rt 12.34 min.); M/Z 73 (100), 103 (20.3), 129 (21.8), 147 (50.5), 191 (31.0) 204 (11.3), 217 (58.3), 259 (12.3), 362 (7.1, M+-TMSOH).

Gluconolactone : (rt 13.62 min); M/Z 73 (100), 129 (20.5), 147 (32.5), 204 (16.6) 217 (11.4), 220 (17.8), 319 (41.0), 361 (5.1, M+-TMSOH -15), 437 (8.4), 466 (4.8, M^+).

Glucose : (rt 14.83 and 21.05 min)

RESULTS AND DISCUSSION

Methyl α-D-glucopyranoside, methyl β-D-glucopyranoside, and anhydrocel-

lobiitol were oxidized with ozone in an aqueous solution at 25°C. The oxidative effects of ozone were assessed by kinetic studies on the ozonolysis of the methyl a-D-and methyl β-D-glucopyranosides, and also by analysis of the products obtained on ozonolysis of anhydrocellobiitol.

Product identification

Retention times of peaks detected on HPLC of the products from ozonolysis of metyhl α-D-glucopyranoside (a-MG), metyl β-D-glucopyranoside (β-MG), and 1, 5-anhydrocellobiitol were coincident with those of oxalic acid, gluconic acid (or glucose), arabinose, glycolic acid, and formic acid as shown in Fig. 2. Arabinolactone as well as the above-mentioned products were proved by GC-MS to be formed from all the three substrates. Anhydroglucitol was detected only in the products from anhydrocellobiitol.

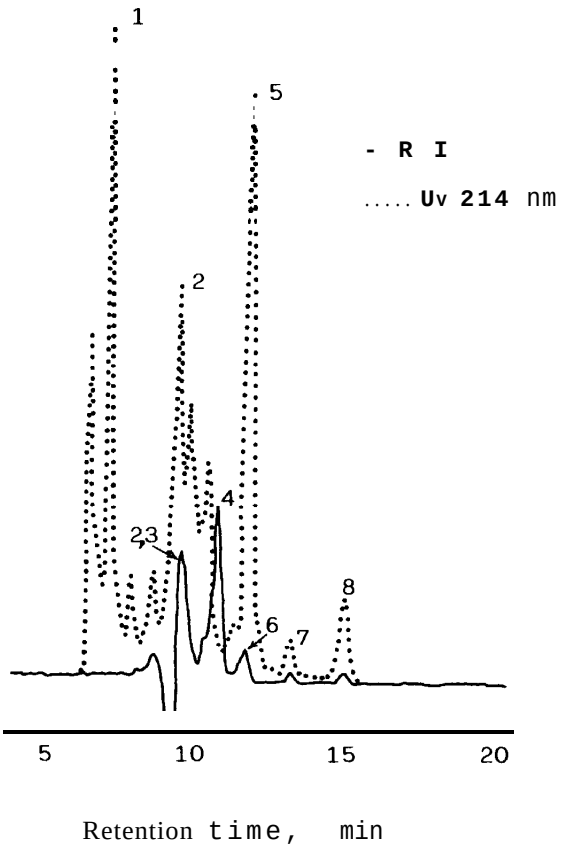

Fig. 2. A typical HPLC chromatogram of ozonolysis products from α-MG reacted for 5 h at 25°C.
Note: 1. oxalic acid; 2. gluconic acid; 3. glucose; 4. α-MG; 5. unknown (arabinonic acid ?); 6. arabinose ; 7. glycolic acid ; 8. formic acid

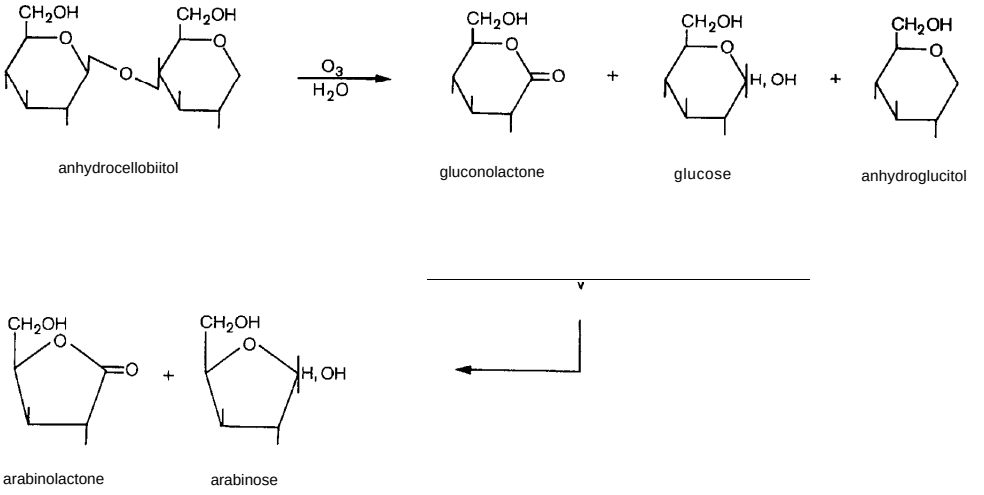

Fig. 3. Proposed pathway for ozonolysis of anhydrocellobiitol.

On the basis of these product analysis, the reaction pathway is proposed for ozonolysis of 1,5-anhydrocellobiitol as shown in Fig. 3. Anhydrocellobiitol afforded glucose, gluconolactone and 1,5-anhydroglucitol as primary products, suggesting that the glucosidic linkage was cleaved both oxidatively and hydrolytically. Similar results were obtained by Nakano's group (Satoh *et al.,* 1984) using cellobiose and lactose as substrates for ozonolysis. Arabinose and arabinolactone can be formed by oxidation and/or decarboxylation of the primary products. These are then further oxidatively degraded to oxalic, glycolic and formic acids. While our results are in agreement with those of Satoh, Ishizu and Nakano (1984), it should be noted that Angineaud et al. (1985) were unable to detect any monosaccharide products from the ozonolysis of cellobiose in aqueous solution, indicating that reaction conditions may be critical.

Kinetics

Orienting ozonolysis experiments were performed at 25°C at a gas flow rate of 220 ml/min, with oxygen which contained 2.5% ozone, using a-MG and β-MG as substrates. The values $ln(S_0/S)$ were plotted against reaction time as shown for several runs in Fig. 4. Here S_0 and S denote the concentration of the substrates before and after reaction, respectively. Plots were practically consistent with pseudo-first order reaction for each run because the coefficient of determination (r^2 value) for each straight line was larger than 0.99. Thus the slopes of those lines can be approximated to apparent rate constants of the ozonolysis runs. It is obvious from Fig. 4 that α- and β-MG were practically stable when oxygen alone was bubbled at the same flow rate as ozonolysis and that β-MG reacted with ozone almost twice as fast as α-MG.

However, it must be noted that the slopes of some of the lines slightly increased when the substrate concentration (S) decreased to about the one fifth of S_0 or less. In other words when $ln(S_0/S)$ increased to 1.5 or more the line slightly deviated from linearity. This suggests that the rate was dependent either on the substrate concentra-

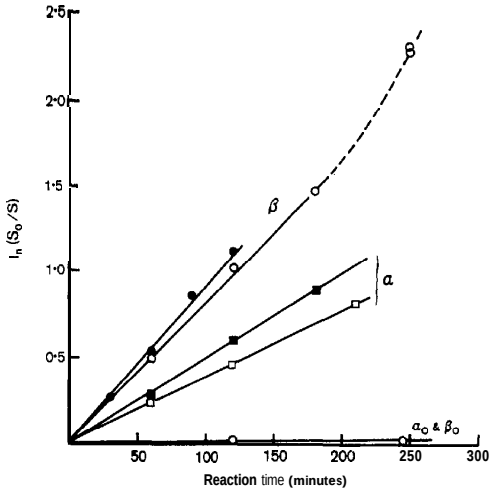

Fig. 4. First order plots for consumption of α-and β-MG by ozone.
Notes : S_o 104 mM, pH controlled, gas flow rate 0.22 ml $\cdot min^{-1}$, α and β with ozone, and α_o and β_o without ozone.

FIG4-5

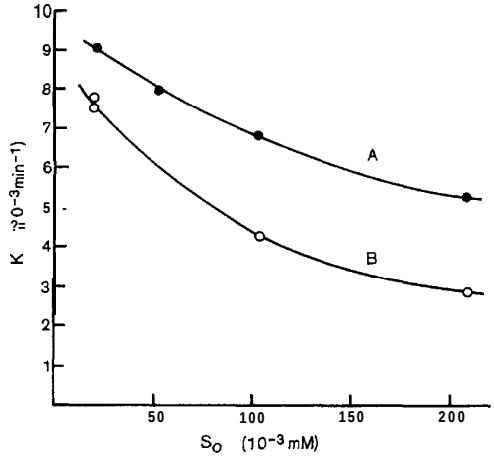

Fig. 5. Influence of initial substrate concentration (S_o) on apparent rate constant (k) of ozonolysis of α-MG at different rates of gas flow 0.35 (A) and 0.22 (B) 1 $\cdot$ min^{-1}.
Note : Temp $\cdot$ 25°C, pH 2.5.

tion or on the influence of autocatalysts formed during the ozonolysis.

In connection with the effect of substrate concentration, the apparent rate constant (K) of the ozonolysis was determined at two levels of flow rate 220 and 350 ml/min using a-MG as a substrate. As shown in Fig. 5 the values of rate constant (K) increased with decreasing the initial substrate concentrations (S_o) at both of the flow rates and were larger at the faster flow rate than the slower flow rate. This result

leads as to the following mechanism of heterogeneous reactions between gas (ozone) and liquid (a substrate solution) phases :

1. The reaction rate is first order both with respect to the concentrations of substrate and dissolved ozone, and
2. The concentration of ozone dissolved in the reaction mixture reached a steady state immediately after start of the ozonolysis, since the rate of ozone consumption becomes equal to the rate of ozone transfer from gas phase to liquid phase by diffusion because of the limited diffusion rate of ozone.

According to these two mechanisms, a reaction which started with a larger S_0 and at a lower rate of gas flow should result in a smaller ozone concentration and, consequently, in a slower reaction rate. The two mechanisms were likely to be valid in our case, since our data in Fig. 5 agreed with the expected phenomena as described above.

Autocatalysis of ozonolysis resulting from the presence of organic acids is unlikely to be the main cause of the observed deviation, although the dependence of ozonolysis rate on pH has been reported by some authors (Mbachu et ***al.,*** 1981a and 1981b; Kamishima et al., 1982 ; Pan ***et al.,*** 1981; Satoh ***et al.,*** 1984), and is well recognized. However, in our studies the apparent rate constant was not substantially influenced by the addition of organic acids (oxalic or formic acids) to the reactant solution, and thus changing the pH of the reaction mixture to about 2.5. Although these acids were detected by HPLC analysis of ozonolysis products, their presence did not account for the observed deviation from linearity.

It was qualitatively observed by Pan et al. (1981) that β-MG reacted almost twice as fast as a-MG, though they did not report the exact ratio values of their reaction rates for these compounds. We measured the ratio of the rates by carrying out the ozonolysis of a mixture of β- and α-MG. Under these conditions straight lines were also obtained for both of the substrates until about two-thirds of β-MG has reacted. The average pseudo-first order constants were 4.1×10^{-3} and 7.3×10^{-3} min^{-1} for α- and β-MG respectively, as shown in Table 1. This means that β-MG reacted 1.8 times as fast as a-MG.

On the basis of kinetic data described above, the rate-determining step should be the first step (see Fig. 1) at which ozone attacks the glucosidic linkage to form an intermediate trioxide or tetroxide (Pan ***et al.,*** 1981), since the kinetic data were first order with respect the substrate and ozone, and the rate constant was dependent **on** the

Table 1. Simultaneous ozonolysis of a-and β-MG

Reaction time (min)	Pseudo-1st order rate const., k (10^{-3} min^{-1}) a-MG	β-MG	k_β/k_α
25	4.0 to.4	7.4±0.5	1.9
60	4.0±0.6	7.4±0.9	1.8
150	4.1±0.1	7.2±0.05	1.8
197	4.4±0.05	7.4i0.2	1.7

Note : Temp. 25°C, gas-flow rate 0.22 l . min^{-1}, and each substrate concn. 52 mM.

configuration of the glucosidic carbon atom (Table 1).

CONCLUSIONS

(1) These studies on the ozonolysis of methyl a-n-glucopyranoside, and anhydrocellobiitol, in aqueous solution at 25°C showed that :

1) The reactin products from the ozonolysis of the α- and P-methyl glucosides were formic acid, glycolic acid, oxalic acid, gluconolactone, glucose, arabinose and arabinolactone.

2) The ozonolysis of anhydrocellobiitol gave glucose, gluconolactone and 1, 5-anhydroglucitol as primary products, indicating that the glucosidic linkage is cleaved both oxidatively and hydrolytically.

3) The rate-determining step in ozonolysis of the glucosides should be the first step at which ozone attacks the glucosidic linkage to form an intermediate trioxide or tetroxide.

4) The ozonolysis rate of methyl β-D-glucopyranoside was 1.8 times as fast as that of methyl α-D-glucopyranoside.

(2) The above results show that ozone attack causes both hydrolysis and oxidation of β-glycosidic linkage, which is the principal feature of cellulose and other pulp carbohydrates.

(3) The results obtained emphasize the well known tendency of ozone to attack and degrade pulp carbohydrates and suggest that in conventional pulp bleaching, better strategies are required for chlorine substitution than its direct replacement by ozone.

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