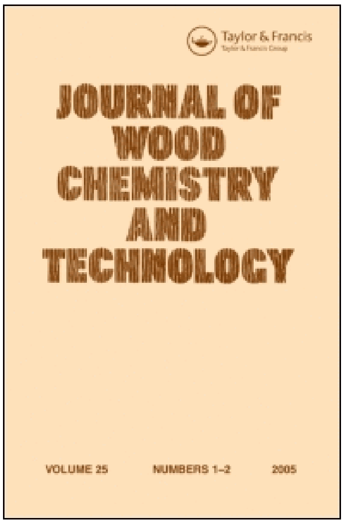

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THE EFFECT OF COBALT ON THE DEGRADATION OF METHYL β-D-GLUCOPYRANOSIDE BY OXYGEN IN AQUEOUS SODIUM HYDROXIDE SOLUTION

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ABSTRACT

The effect of Co(II) (0 to 0.25 mM $CoSO_4$) on the degradation of methyl β-D-glucopyranoside (MBG) at 120°C in 1.25M NaOH with 0.68 MPa oxygen pressure was studied. When the Co(II) was increased from 0.00 to 0.01 to 0.05 mM the MBG half-life decreased from 12 to 6 to 1.5 hours, reflecting approximately a 0.5 order kinetic dependence on cobalt. An oxidation-reduction cycle between Co(II) and Co(III) involving oxidation of Co(II) by oxygen and oxidation of the glucoside by Co(III), hydroxyl radical, or superoxide is proposed for the degradation. At the 0.25 mM Co(II) addition level highly adsorptive $Co(OH)_2$ formed prior to reaction initiation with oxygen and removed otherwise soluble cobalt from solution. This resulted in lower rates of MBG degradation than obtained even at 0.01 mM Co(II) addition. However, Co(II) solubility could be enhanced if silicate anions or polyols (including MBG) were added to the alklaine medium prior to the Co(II) addition. In reactions initially containing 0.25 mM soluble Co(II), an adsorptive precipitate, presumably CoO(OH), gradually formed after reaction initiation with oxygen. Precipitation of the Co(III) solid coincided with a rapid decline in the rate of MBG degradation. Cobalt had little effect on the products of MBG degradation.

INTRODUCTION

In oxygen-alkali delignification processes trace quantities of transition metal ions can induce extensive carbohydrate degradation[1]. However, reduced carbohydrate degradation can also be afforded by an excess of the same transition metal ions which promote extensive degradation in trace quantities [Fe[2], Co[1,3,4], Mn[2,5]]. This study examines the relationship between initial Co(II) concentration and degradation of methyl β-D-glucopyranoside (MBG) with oxygen in aqueous sodium hydroxide solutions.

RESULTS AND DISCUSSION

Two NaOH solutions were used in this work; "extracted" NaOH, prepared via complexation and extraction of transition metal ions[6], and commercial "ultrapure" NaOH[7]. The extracted NaOH contained silicate and borate introduced by contact with Pyrex glassware during preparation.

The rate of MBG degradation at 0.68 MPa oxygen pressure in 1.25M NaOH at 120°C was the same in either extracted or ultrapure NaOH (Fig. 1, reactions 1 and 2). The rate of reaction was accel-

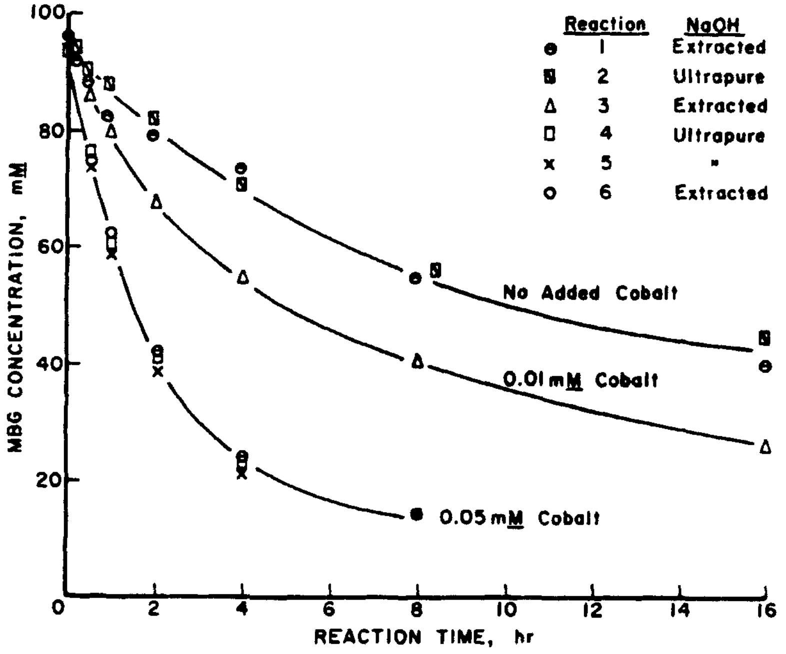

Figure 1. Degradation of Methyl β-Glucopyranoside in 1.25M NaOH with 0.68 MPa Oxygen at 120 C; 0.00, 0.01, and 0.05mM $CoSO_4$ Addition.

erated by 0.01 m$\underline{M}$ and 0.05 m$\underline{M}$ Co(II) in extracted NaOH (Fig. 1, reactions 3 and 6). At 0.05 m$\underline{M}$ Co(II) the rate of MBG degradation was essentially the same in either extracted or ultrapure NaOH (Fig. 1, reactions 4, 5, and 6). The MBG degradation rate exhibited approximately 0.5 order kinetic dependence on cobalt.

For MBG degradations with 0.25 m$\underline{M}$ Co(II) in ultrapure NaOH, $Co(OH)_2$ precipitated from the alkaline solution prior to reaction initiation. The precipitation of Co(II) from ultrapure NaOH solution resulted in the rate of MBG degradation at 0.25 m$\underline{M}$ cobalt addition being less than that at 0.01 m$\underline{M}$ Co(II) (Fig. 2, reactions 7 and 8).

The precipitation of Co(II) from ultrapure NaOH solutions at 0.25 m$\underline{M}$ Co(II) addition resulted in the total loss of blue color associated with alkaline solutions of Co(II)[8]. This suggests that

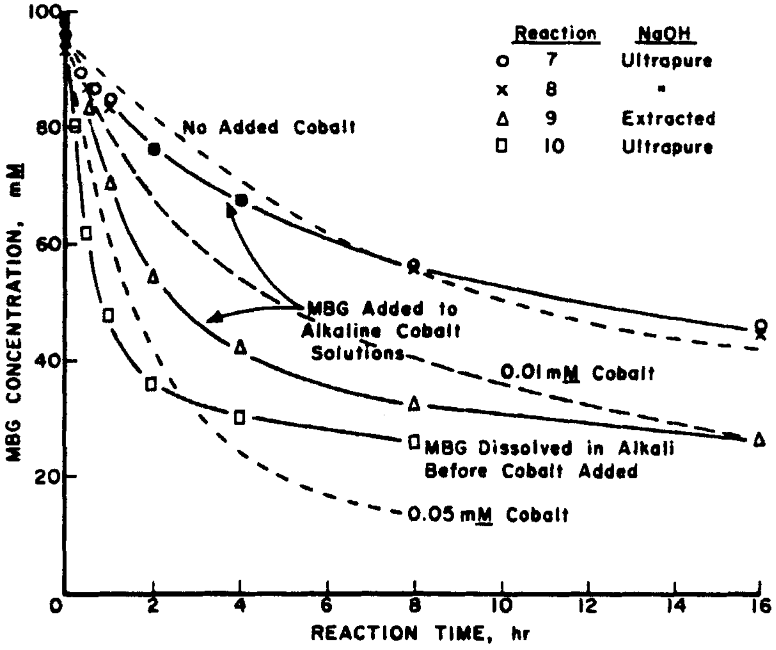

Figure 2. Degradation of Methyl β-Glucopyranoside in 1.25$\underline{M}$ NaOH with 0.68 MPa Oxygen at 120°C; 0.25 m$\underline{M}$ $CoSO_4$ Addition

the $Co(OH)_2$ which precipitates from solution can adsorb otherwise soluble cobalt ions from solution. Atomic absorption analysis of alkaline (1.25<u>M</u> ultrapure NaOH) solutions of $CoSO_4$ confirmed the adsorptive ability of the Co(II) precipitate. After 24 hours at room temperature in the absence of oxygen, solutions which were initially 0.05, 0.25, and 0.83 m<u>M</u> $CoSO_4$ were filtered and were found to contain 0.05, 0.02, and 0.01 m<u>M</u> soluble cobalt, respectively.

The initial rate of MBG degradation at 0.25 m<u>M</u> Co(II) addition was substantially increased if the alkaline solution contained silicate anions. MBG degraded at a much faster rate in extracted NaOH than in ultrapure NaOH at 0.25 m<u>M</u> Co(II) (Fig. 2, reactions 7, 8, and 9). The accelerated rate of MBG degradation can be attributed to enhanced solubility of Co(II) in the alkaline solution by silicate anions. The ability of silicate anions to enhance Co(II) solubility in alkaline solution was investigated by mixing alkaline sodium silicate ($Na_2SiO_3 \cdot 9H_2O$) solutions with cobalt ($CoSO_4 \cdot 7H_2O$) solutions so that the cobalt was in excess of that soluble in the alkali alone. Since Co(II) solubility increases with increasing alkalinity[9], solutions were prepared to be 3.3<u>M</u> in NaOH to facilitate analysis of the cobalt. Cobalt(II) which precipitated upon mixing of the cobalt and alkaline silicate solutions was removed by centrifugation, and the absorbance of the supernatant was determined at 585 nm. Silicate anions clearly enhance Co(II) solubility in alkaline solution (Table 1). Silicate intensified the absorbancies, but did not shift the absorption maxima (535, 585, and 625 nm) of the alkaline Co(II) solutions. Intensification of the absorbance (585 nm) also coincided with a decrease in precipitate formation, indicating that the silicate anions are capable of coordinating with Co(II) under strongly alkaline conditions.

Similar experiments using sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) showed that borate anions do not enhance Co(II) solubility in alkaline solution.

TABLE 1

Effects of Sodium Silicate on Cobalt(II)[a] Solubility in Alkaline Solution

Solution Composition		
NaOH, M	$Na_2SiO_3 \cdot 9H_2O$, mM	Absorbance 585 nm
0.0	71.0	0.064
3.3	0.0	0.098
3.3	7.1	0.242
3.3	12.0	0.325
3.3	36.0	0.394[b]

[a] $CoSO_4 \cdot 7H_2O$ addition equivalent to 2.08 mM.
[b] No precipitate formed during solution preparation.

The initial rate of MBG degradation with 0.25 mM initial Co(II) could be substantially increased in ultrapure NaOH (no silicates) if the reaction solution preparation procedure was reversed. The addition of Co(II) solution to an alkaline MBG solution (Fig. 2, reaction 10) as opposed to addition of solid MBG to an alkaline Co(II) solution (Fig. 2, reactions 7 and 8), enhanced Co(II) solubility and resulted in a very rapid initial rate of MBG degradation.

The ability of MBG and other polyols (sorbitol, glycerol, and ethylene glycol) to enhance Co(II) solubility in alkaline solution was also demonstrated spectrophotometrically. The results are summarized in Table 2. In each case the polyol caused the absorbance due to soluble Co(II) to increase.

In reactions in which 0.25 mM Co(II) was initially soluble (Fig. 2, reactions 9 and 10), Co(III), presumably as CoO(OH), gradually precipitated from solution after reaction initiation by oxygen pressurization. No cobalt precipitation was evident in reactions with 0.01 and 0.05 mM Co(II). Following precipitate formation in reactions containing 0.25 mM Co(II) initially, the rate of MBG degradation decreased very rapidly. In the reaction in which MBG degraded at the greatest initial rate (Fig. 2, reac-

TABLE 2

Effect of Polyols on Cobalt(II)[a] Solubility in 3.3M NaOH

Polyol	Absorbance 585 nm
None	0.098
0.1M Ethylene glycol	0.165
0.1M Sorbitol	0.284
0.1M Glycerol	0.389[b]
0.1M MBG	0.385[b]

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[a] $CoSO_4 \cdot 7H_2O$ addition equivalent to 2.08 mM.
[b] No precipitate formed during solution preparation.

tion 10), the degradation of MBG was less after 4 h than in the initially slower degradations with 0.05 mM initial Co(II).

Cobalt(III) which precipitated during MBG degradations at the 0.25 mM Co(II) level (Fig. 2, reactions 9 and 10) was also highly adsorptive. Adsorption of soluble cobalt by the precipitated Co(III) resulted in a drastically decreased rate of MBG degradation after *ca.* 1 h of reaction, (Fig. 2, reaction 9), and a substantial decrease in the cobalt remaining in solution after reaction termination. Initial Co(II) charges *versus* the final soluble cobalt concentrations were, in mmoles/l; 0.01 *vs.* 0.007 (reaction 3), 0.05 *vs.* 0.039 (reaction 6), and 0.25 *vs.* < 0.0008 (reactions 7 and 9), and 0.25 *vs.* 0.0037 (reaction 10). Thus, the greatest initial cobalt ion concentrations resulted in the lowest final soluble cobalt levels.

Under conditions for which no initial precipitation of cobalt occurred, the rate of MBG degradation at the 0.25 mM Co(II) addition level was slower in NaOH containing silicate (reaction 9) than in ultrapure NaOH (reaction 10), suggesting that silicate anions acted as inhibitors of MBG degradation at the 0.25 mM Co(II) addition level in initially homogeneous reaction solutions. In addition, since the quantity of precipitate formed in NaOH containing silicate was noticeably greater than in ultrapure NaOH after *ca.* 1 h of reaction, the silicates, while inhibiting Co(II) precipitation in alkaline solution, may also have promoted the oxidative precipitation of Co(III) during MBG degradation. Silicate monomers have been noted to form complexes with Fe(III)[10] while also promoting the oxidation of Fe(II) to Fe(III)[11]. With Co(II) initially 0.05 m*M*, silicates did not influence the rate of MBG degradation (Fig. 1, compare reactions 4, 5, and 6), probably because Co(III) did not precipitate. Silicates did not coprecipitate with cobalt. The amorphous precipitate from MBG degradation in NaOH containing silicate and initially 0.25 m*M* cobalt was analyzed by energy dispersive X-ray analysis and no element other than cobalt with molecular weight greater than sodium was evident.

Metal ion precipitation under oxygen-alkali conditions has been associated with a decrease in carbohydrate degradation[1-5], but the connection between reaction rate and adsorptive precipitate formation has not been clearly established. However, the ability of freshly precipitated metal oxides and hydroxides to adsorb soluble metal ions from solution is well recognized under neutral and slightly alkaline conditions for precipitates of manganese[12,13] and iron[14]. Indeed, the most plausible explanation for the ability of precipitated magnesium hydroxide to inhibit carbohydrate degradation in oxygen-alkali is adsorption of catalytic transition metal impurities[15,16]. The mechanism of adsorption of soluble metal species at the solid oxide or hydroxide-solution interface at high alkalinities appears to be complicated and is not understood[17,18]. It is likely, however, that both precipitated Co(II) and Co(III) absorb cobalt ions by comparable mechanisms since metal oxides can hydrate at the surface and convert to surface hydroxides[19].

Although soluble cobalt ions accelerated the rate of MBG degradation, the presence of cobalt ions in reaction solutions had a relatively minor influence on the products of MBG degradation. Methanol formation, indicative of glycosidic bond cleavage, accounted for *ca*. 70 mole percent of reacted MBG regardless of the cobalt concentration. Similarly, the acidic products produced during MBG degradation were the same in the presence or absence of added cobalt, in agreement with Ericsson et al.[20].

The mechanism in Fig. 3 is proposed to account for the observed catalytic ability of cobalt ions during MBG degradation. The addition of alkali to an aqueous Co(II) solution results either in the precipitation of $Co(OH)_2$, or in the formation of $Co(OH)_3(H_2O)^-$ and $Co(OH)_4^{2-}$. An increase in alkalinity, or the presence of silicates or coordinating polyols shifts the equilibrium in favor of soluble ionic Co(II). As demonstrated in this work, the precipitation (in the absence of oxygen) of Co(II) from an alkaline solution supersaturated with respect to cobalt can result in the formation of a highly adsorptive precipitate. The precipitated $Co(OH)_2$ is readily oxidized by oxygen to produce a hydrous Co(III) oxide precipitate[21]. Coordinating species can enhance the solubility of Co(III) in oxidative alkaline solution and an oxidation-reduction cycle between Co(II) and Co(III) may be established. A highly adsorptive Co(III) precipitate may also form from the alkaline solution. Silicate anions, while enhancing

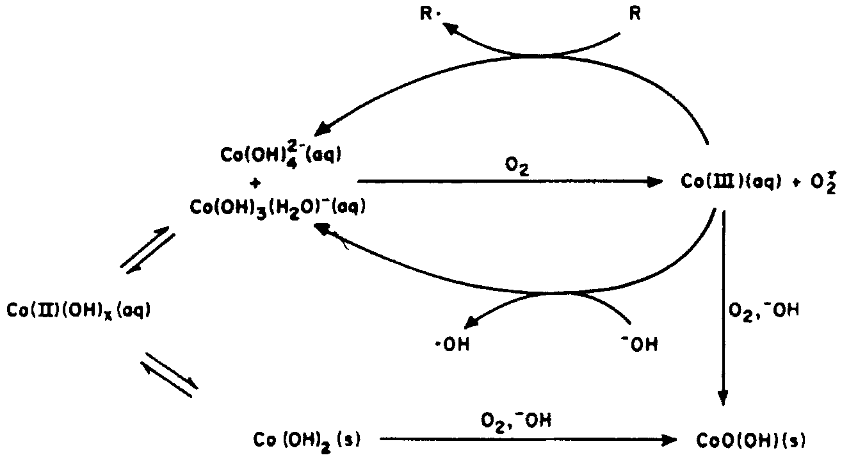

Figure 3. Proposed Pathways of Cobalt-Catalyzed Carbohydrate Degradation and Free Radical Generations

Co(II) solubility in alkaline solution, presumably promote oxidative precipitation of Co(III) from the solution.

Under acidic conditions Co(II) can react directly with oxygen to produce Co(III) and hydroperoxy radical (HOO·)[22,23]. It is likely that a similar reaction occurs under oxidative alkaline conditions with the production of superoxide radical as in Fig. 3. Also under acidic conditions, Co(III) is known to react with hydroxyl ion to produce hydroxyl radical, although direct oxidation of an organic substrate by Co(III) is more favorable[24-26]. Under alkaline conditions similar reactions of Co(III) would probably occur. Direct Co(III) oxidation of carbohydrates in oxygen-alkali is supported by the fact that methanol was degraded in an oxygen-alkali-cobalt system, but not in an oxygen-alkali system[27]. The yellow color which developed in cobalt-containing reaction solutions after reaction initiation by oxygen pressurization was attributable to the formation of a stable Co(III) complex (or complexes) with MBG degradation products. The yellow color intensified with reaction time but decreased upon precipitation of Co(III) from reaction solutions. Reaction solutions not containing cobalt remained colorless.

The oxidation of a substrate by a metal ion that exists in two (or more) oxidation states, followed by rapid reoxidation of the metal ion by molecular oxygen commonly serves as a basis for a catalytic system[28,29]. Thus, a catalytic cycle between Co(II) and Co(III) which promotes free radical degradation of MBG seems quite plausible. The catalytic cycle is complicated, however, by adsorptive precipitate formation under both anaerobic and aerobic conditions, and by complexation of cobalt with species such as silicate anions and the carbohydrate substrate (MBG). The importance of competing complexation of cobalt by MBG degradation products requires further investigation.

EXPERIMENTAL

Methyl β-D-glucopyranoside (Pfanstiehl Laboratories, Waukegan, IL) was refluxed in 1.0*M* NaOH for 1 h to remove traces of reducing sugars, deionized, and recrystallized twice from ethanol. The MBG was chromatographically pure[30]. Extracted NaOH was prepared by a procedure using phenyl-2-pyridyl ketoxime to remove trace metal contaminates[6]. Contact of the NaOH with Pyrex glassware resulted in the extracted NaOH solutions containing 500 ppm Si, 250 ppm B, and 13 ppm Al. Ultrapure NaOH solutions contained less than 0.5 ppm combined Si, B, and Al. The total concentration of Cd, Cr, Cu, Fe, Mg, Mn, and Ni was less than 0.7 ppm in all reactions. Metal concentrations were determined by inductively coupled argon plasma emission analysis (Trace Elements Inc., Park Ridge, IL).

The reactor consisted of a teflon-lined brass bomb (*ca.* 250 mL capacity) equipped with an air-driven magnetic stirrer[30-32]. The reactor (maintained at 120 ± 0.2°C in an oil bath) could be sampled repeatedly through an inert valve system while hot and under pressure.

Reaction solutions were prepared by mixing 10 mL of a stock aqueous $CoSO_4 \cdot 7H_2O$ solution with 240 mL of an NaOH solution such that the final NaOH concentration was 1.25*M*. MBG was added to the alkaline Co(II) solutions as a solid except in reaction 10, where it was dissolved in the stock alkaline solution prior to mixing with aqueous $CoSO_4 \cdot 7H_2O$. Stock NaOH solutions were carbonate-free, and water was triply distilled and carbon-dioxide free[30].

The reactor was loaded and sealed under a nitrogen atmosphere, heated to reaction temperature (120°C), and reactions were initiated by oxygen pressurization [0.68 MPa (25°C)]. Samples were periodically collected, and analyses were conducted for unreacted MBG, methanol, and selected acidic products.

Remaining MBG was determined by glc of acetylated samples using *n*-butyl β-*D*-glucopyranoside as an internal standard. Acetylation and glc analyses followed the procedures reported by Millard *et al.*[32].

Samples for methanol analysis were analyzed directly by glc, based on the technique reported by Sims[33] using ethanol as an internal standard. The column (stainless steel, 4 ft x 0.125 inch) was rigged for off-column injection and packed with 5% Carbowax 20M on 80/100 mesh Chromosorb 101. Analysis conditions were: nitrogen, 35 mL/min; column, 70°; injector, 120°; and detector, 260°.

Acidic products were analyzed by glc as their pertrimethylsilyl ethers. The products were identified on the basis of relative retention times and glc-ms analysis[20,34].

Visible spectra were obtained on a Perkin-Elmer 576 ST spectrophotometer. Alkaline cobalt solutions containing silicates, borates, or polyols were all prepared in the same manner. To 1 mL of 10M NaOH in a 5 mL volumetric flask which was continuously purged with nitrogen through a capillary tube, was added 1 mL of an aqueous stock solution containing the additive of interest (silicates, borates, or polyol). To this mixture was added 1 mL of 6.25 mM $CoSO_4 \cdot 7H_2O$. Stock silicate solutions (0.021, 0.036, 0.108, 0.213M) were prepared with sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$). A stock borate solution was prepared to be 0.210M in sodium borate ($Na_2B_4O_7 \cdot 10H_2O$). Stock polyol solutions were: 0.303M MBG; 0.300M sorbitol; 0.303M glycerol; and 0.303M ethylene glycol. Samples were centrifuged (2000 rpm, 5 min) to remove unsettled precipitate, and visible spectra of the supernatant solutions were immediately recorded.

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