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RESEARCH ARTICLE

Hydrogen peroxide decomposition in bicarbonate solution catalyzed by cobalt (II)

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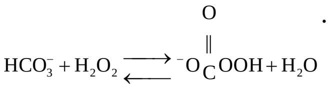
Abstract

The peroxymonocarbonate mono- and di-anions (HCO_4^- and CO_4^{2-}) are known to be generated from H_2O_2/HCO_3^-. They are promising oxidants for wood pulp bleaching, but peroxide decomposition catalyzed by Co(II) species is more significant when unusually high Co concentrations are present in pulp, though Co is usually ≤ 0.1ppm in wood pulps. This investigation aimed to see if H_2O_2 could abstract an electron from transition metal species with a lower oxidation than the -0.67 reported for $Mn(HCO_3)_2$. Peroxide decomposition catalyzed by Co(II) was investigated in H_2O_2/HCO_3 in the pH range 8.5 – 8.7. The rate equation for peroxide decomposition was first order in $[H_2O_2]$ in the pH range studied. At $[HCO_3^-] > 0.025M$, Co(II) catalysis of the hydrogen peroxide was retarded. A tentative ionic mechanism is proposed to explain the hydrogen peroxide decomposition.

Introduction

It has been known that hydrogen peroxide reacts with the bicarbonate anion to generate the peroxymonocarbonate mono-anion (HCO_4^-) (Flanagan et al., 1986; Richardson et al., 2000; Bennett et al., 2001). The equilibrium reaction and equilibrium constant associated with HCO_4^- formation are given by (1) and (2) (Flanagan et al., 1986).



$$HCO_3^- + H_2O_2 \rightleftarrows {}^-O\overset{\overset{O}{\|}}{C}OOH + H_2O \qquad \text{........................1}$$

$$K = 0.32M^{-1} = \frac{[HCO_4^-]}{[H_2O_2][HCO_3^-]} \qquad \text{....................... 2}$$

The peroxymonocarbonate (PMC) mono-anions dissociate to form the di-anion (CO_4^{2-}) with a pKa of about 10.0 (Flanagan et al., 1986; Richardson et al., 2000; Bennett et al., 2001; Attiogbe et al., 2010a; Attiogbe et al., 2010b; Vakhitova et al., 2006). Results were recently reported where the two anions showed great promise as bleaching agents for wood pulps (Attiogbe et al., 2010a; Attiogbe et al., 2010b). The results appear to indicate that the mono-anion is electrophilic while the di-anion is nucleophilic, and both classes of reaction occur about the pH of 8.5 (Attiogbe et al., 2010a; Attiogbe et al., 2010b). The use of peroxide/bicarbonate (P_B) bleaching in conjunction with a non-sulfur alkaline pulping process such as soda/anthraquinone is particularly attractive. In such a situation the pulping effluent would be concentrated by evaporation and incineration to give a Na_2CO_3 or K_2CO_3 stream of high purity. It has already been shown that a mole of carbonate in solution reacts quite quickly with a mole of CO_2 at low pressure to generate two moles of bicarbonate (Attiogbe et al., 2010a; Attiogbe et al., 2010b). Therefore, P_B bleaching is possible without the purchase of carbonate or bicarbonate, if the P_B effluent were to be recycled to the pulping chemical recovery system and Na_2CO_3 or K_2CO_3 recycled back to the P_B stage. Carbon dioxide may be obtained from the flue gas associated with combustion of the concentrated pulping and bleaching effluents.

One problem that has to be solved is the development of stabilization strategies to minimize the decomposition of peroxide catalyzed by Fe and Mn species during a P_B stage (Attiogbe and Francis, 2011a; Attiogbe and Francis, 2011b). Earlier data clearly showed that these two transition metals catalyze peroxide decomposition significantly in the bleaching slurry and that such decomposition could be retarded to a very high degree by the addition of an effective scavenger for the hydroxyl radical (Attiogbe et al., 2010a; Attiogbe et al., 2010b). When $Fe_2(SO_4)_3$ or $MnSO_4$ was added to bleaching effluent containing H_2O_2, the inclusion of N, N'-(5-nitro-1, 3-phenylene)-bisglutaramide (GAMID) as a hydroxyl radical scavenger (Attiogbe and Francis, 2011a; Singh and Hider, 1988; Zhang et al., 1998) decreased the rate of peroxide decomposition by a factor of at least ten for both Fe(III) and Mn(II). In addition to wasteful decomposition of H_2O_2, a second and probably greater concern is that $\cdot OH$ is generated at a moderate to high rate by Fe (III) and Mn (II) catalysis. This free radical can retard the brightening of mechanical pulps (Gierer et al., 1993) and lower the degree of polymerization of the cellulose in chemical pulps to unacceptable levels (Francis et al., 1994).

Reactions of cobalt(II) compounds with hydrogen peroxide in a weakly alkaline medium have been established to not forming hydroxyl radicals in intermediate stages of the reactions (Lunenok-Burmakina et al., 1981). Hydrated cobalt (II) ions in a weakly alkaline medium in the presence of hydrogen peroxide are reported to be rapidly oxidized to Co (III) compounds. Catalytic decomposition of hydrogen peroxide is reported to occur in this situation. The O-O bond in hydrogen peroxide is reported to be transformed to O_2 without cleavage upon such a catalytic decomposition Lunenok-Burmakina et al., 1981).

The objective of this paper is to report recent findings of H_2O_2 abstraction of an electron from transition metal species with a lower oxidation than the -0.67 reported for $Mn(HCO_3)_2$ (Attiogbe and Francis, 2011a). Co(II) presents in wood pulps, though usually ≤ 0.1ppm was investigated since coupling its half-reaction with equation (3) would be endoergic by 1.46V.

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \qquad 0.46\text{V} \qquad (3)$$

$$Co^{2+} \rightarrow Co^{3+} + e^- \qquad -1.92\text{V}^{*}\ [13] \qquad (4)$$

$$H_2O_2 + Co^{2+} \rightarrow Co^{3+} + \cdot OH + OH^- \qquad -1.46\text{V} \qquad (5)$$

This paper investigated Co(II) catalysis of peroxide decomposition in $NaHCO_3$ solutions at pH range of 8.5–8.7 and temperature of 40°C.

Materials and Methods

All the procedures were similar to those described in (Attiogbe and Francis, 2011a; Attiogbe and Francis, 2011b). The salt used was 99+% extra pure cobalt(II) sulfate heptahydrate (Acros Organics).

Results and Discussion

Co(II) was very catalytic and afforded decomposition rates that were higher than those of Fe(III) and Mn(II). When 0.1ppm Co(II) was used (no citrate) in 0.1M HCO_3^- with pH range of 8.5 – 8.7, duplicate rate constants (k_{OBS}) of $6.5\times10^{-4}\ s^{-1}$ and $6.7\times10^{-4}\ s^{-1}$ were obtained. The rate constant for 0.1ppm Mn(II) under similar conditions was $1.6\times10^{-4}\ s^{-1}$ (Attiogbe and Francis, 2011b) while the value for 0.1ppm Fe(III) complexed with citrate was $6.4\times10^{-4} s^{-1}$ (Attiogbe and Francis, 2011a).

Only a preliminary investigation of Co(II) was performed because it is normally present in wood pulps at ≤ 0.1 ppm and not much of it desorbs during the bleaching process, (see Table 1). The investigation was initiated with 0.05ppm and 0.1ppm Co(II) without citrate complexation. The first order plots in terms of $[H_2O_2]$ are presented in Figure 1 for various [Co(II)] and $[HCO_3^-]$ while the rate constants are tabulated in Table 2. The rate constant was computed using equation (6). The rate constant for H_2O_2 decomposition in 0.1M HCO_3^- (pH 8.5 – 8.7) doubled from $3.3\times10^{-4}\ s^{-1}$ to $6.6\times10^{-4}\ s^{-1}$ when [Co(II)] increased from 0.05ppm to 0.1ppm. This is indicative of a first order dependence on [Co(II)].

$$\frac{d[H_2O_2]}{dt} = -k_{OBS}[H_2O_2] \qquad [6]$$

Fig. 1. First-order plots in terms of $[H_2O_2]$ for peroxide decomposition catalyzed by Co(II) in 0.1 mol/L HCO_3^- at 40 °C and pH 8.5 – 8.7. No citrate was added.

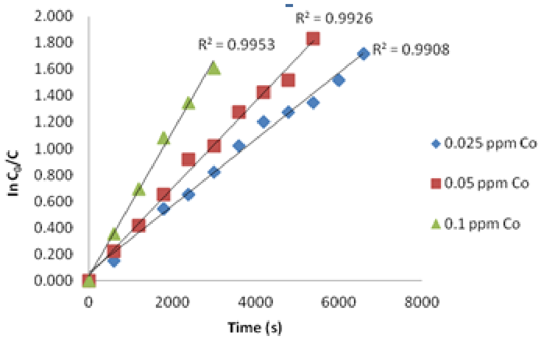


Table 1. Transition and Alkaline Earth Metals in 100% Commercial Aspen CTMP before and after Q Stages.

Metal	Untreated Pulp	Q_1-treated	Q_1Q_2-treated
Mg	355	55	62
Cu	8.3	4.9	5.2
Mn	11.3	3.2	0.5
Fe	29.0	8.7	8.6
Co	0.07	0.06	0.07

Note: Q-stage (Chelation) using Na_5DTPA and or $Na_5DTPMPA$ and $NaHSO_3$; CTMP-Chemi thermomechanical pulp

The reaction order determination for [HCO_3^-] was initiated with concentrations of 0.5 ppm Co(II) and 0.05M HCO_3^-. The rate constant actually increased from 3.3×10^{-4} s^{-1} to 5.9×10^{-4} s^{-1} when the [HCO_3^-] was decreased from 0.1M to 0.05M. Lower [HCO_3^-] were investigated and it showed that k_{OBS} increased with [HCO_3^-] in the range of 0.005M to 0.025M then started decreasing as [HCO_3^-] is increased further. The rate constants are documented in Table 2 along with the initial and end pH as [HCO_3^-] was increased. There is an increase in the decomposition rate as initial pH is increased from 7.8 to 8.3. The pH increase was due to increasing [HCO_3^-] from 0.005M to 0.025M. When the [HCO_3^-] was increased further, initial pH increased from 8.3 at 0.025M to 8.4 at 0.05M and 8.5 at 0.10M. However, it appeared that high [HCO_3^-] retarded Co(II) catalysis thus k_{OBS} started decreasing at [HCO_3^-] > 0.025M. A possible explanation is that dissociation of HCO_3^- to CO_3^{2-} became significant at pH 8.3; two units lower than the pKa of HCO_3^-. Retardation of Co(II) catalysis could be due to the formation of insoluble $CoCO_3$, a compound with a K_{SP} value of only 1.4×10^{-13}. It also appears that citrate addition lowered the decomposition rate (Table 2).

Table 2. First order rate constants for Co(II) catalyzed peroxide decomposition in HCO_3^- solutions [according to equation (6)][1]

[Co(II)], ppm	[HCO_3^-], M	Citrate Addition[2]	Initial pH[3]	End pH	$k_{OBS,}$ $s^{-1}(\times10^{-4})$
0.05	0.005	N	7.8	8.0	2.7
0.05	0.01	N	8.1	8.3	6.1
0.05	0.025	N	8.3	8.4	8.2
0.05	0.05	N	8.4	8.5	5.9
0.05	0.10	N	8.5	8.6	3.3
0.05	0.10	Y	8.5	8.6	3.1
0.10	0.10	N	8.5	8.6	6.6
0.10	0.10	Y	8.5	8.6	5.6

[1] 50 mM H_2O_2 at 40°C
[2] N = no; Y = yes
[3] Taken at 0 minute after the addition of all chemicals

The mechanism in equations (7) – (11) is tentatively proposed to explain peroxide decomposition in accordance with the experimental data. The mechanism is ionic in nature and it is assumed that a free radical scheme involving Co(II) being oxidized to Co(III) is highly unlikely. The oxidation of Co(II) to Co(III) by hydrogen peroxide is endoergic by 1.46 V [combination of equations (3) and (4)]. Equation (7) is primary to this tentative mechanism and the pKa of Co(II) in the reaction is about 9.7 (Baes and Mesmer, 1976; Giasson and Tewari, 1978).

$$Co^{2+} + H_2O \xleftrightarrow{K_1} CoOH^+ + H^+ \qquad (7)$$

$$CoOH^+ + H_2O_2 \xrightarrow{k_2} Co(OOH)^+ + H_2O \qquad (8)$$

$$Co(OOH)^+ + OH^- \xrightarrow{k_3} Co(OOH)(OH) \qquad (9)$$

$$2Co(OOH)(OH) \xrightarrow{k_4} 2CoOH^+ + O_2 + 2OH^- \qquad (10)$$

The rate law for the mechanism is given in equation (Francis et al., 1994) and its derivation is provided in the supplementary data. Based on the rate law and pKa of Co(II) it would be expected that the rate of peroxide decomposition should become significant at a pH of about 7.7 and without Co(II) deactivation should increase with increasing pH until pH reaches around 10. About this pH of 10, the dissociation of $CoOH^+$ to $Co(OH)_2$ slowed, decreasing the [$CoOH^+$] (Giasson and Tewari,1978). The experimental data i.e. increasing decomposition rates in the pH range of 7.8 – 8.3 are consistent with the proposed mechanism. There is a substantial body of evidence from previous research showing that $CoOH^+$ adsorbs to colloidal metal oxides (Fe_2O_3, TiO_2, SiO_2) at a higher rate than does Co^{2+} or $Co(OH)_2$ (Matijević, 1967; Matijević and White, 1984; Fuerstenau and Osseo-Asare, 1987). It is therefore possible that $CoOH^+$ would be attracted to one of the pairs of unbonded or unpaired electrons on oxygen atoms in H_2O_2 equation (8).

$$\frac{d[O_2]}{dt} = \frac{K_1 k_2 [Co^{2+}][H_2O_2]}{[H^+]} \qquad (11)$$

Conclusion

Co(II) was an aggressive catalyst for hydrogen peroxide decomposition in 0.1M HCO_3^- and pH 8.5 – 8.7. However, high $[HCO_3^-]$ retarded Co(II) catalysis thus k_{OBS} started decreasing at $[HCO_3^-] > 0.025M$. A tentative reaction mechanism is proposed for Co(II) catalysis. All the cobalt intermediates are in a +2 oxidation state and the observations point to unlikely formation of the Co(II) to Co(III) during the hydrogen peroxide reduction.

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Supplementary Data

$$Co^{2+} + H_2O \xleftrightarrow{K_1} CoOH^+ + H^+$$

$$CoOH^+ + H_2O_2 \xrightarrow{k_2} Co(OOH)^+ + H_2O$$

$$Co(OOH)^+ + OH^- \xrightarrow{k_3} Co(OOH)(OH)$$

$$2Co(OOH)(OH) \xrightarrow{k_4} 2CoOH^+ + O_2 + 2OH^-$$

$$K_1 = \frac{\left[CoOH^+\right]\left[H^+\right]}{\left[Co^{2+}\right]} \Rightarrow \left[CoOH^+\right] = \frac{K_1\left[Co^{2+}\right]}{\left[H^+\right]}$$

$$\frac{d\left[Co(OOH)^+\right]}{dt} = k_2\left[CoOH^+\right]\left[H_2O_2\right] - k_3\left[Co(OOH)^+\right]\left[OH^-\right] = 0$$

$$\left[Co(OOH)^+\right] = \frac{k_2\left[CoOH^+\right]\left[H_2O_2\right]}{k_3\left[OH^-\right]}$$

$$\frac{d\left[Co(OOH)(OH)\right]}{dt} = k_3\left[Co(OOH)^+\right]\left[OH^-\right] - k_4\left[Co(OOH)(OH)\right]^2 = 0$$

$$\left[Co(OOH)(OH)\right]^2 = \frac{k_3\left[Co(OOH)^+\right]\left[OH^-\right]}{k_4} = \frac{k_2\left[CoOH^+\right]\left[H_2O_2\right]}{k_4}$$

$$\frac{d\left[O_2\right]}{dt} = k_4\left[Co(OOH)(OH)\right]^2 = k_2\left[CoOH^+\right]\left[H_2O_2\right] = \frac{K_1k_2\left[Co^{2+}\right]\left[H_2O_2\right]}{\left[H^+\right]}$$