

Stability of hydrogen peroxide in sodium carbonate solutions

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ABSTRACT

The rate of decomposition of hydrogen peroxide has been measured in aqueous, concentrated (0.1–1M) reagent-grade sodium carbonate liquors and compared with that in sodium hydroxide liquors at the same pH, temperature, and ionic strength. Over the ranges of temperature (303–323 K), pH (10.0–10.6), and ionic strength (1.5–3.0M), and without peroxide-stabilizing additives, hydrogen peroxide decomposes about nine times faster in the carbonate liquor than in caustic liquor. In the absence of stabilizing additives, the average first-order reaction rate constant for peroxide decomposition in carbonate liquors was $60 \text{ E-}5 \pm 10 \text{ E-}5 \text{ s}^{-1}$.

Peroxide decomposition in carbonate liquor, which is probably caused by catalytic metal ions, is slowed by conventional alkaline peroxide-stabilizing agents (MgSO_4 , Na_2SiO_3 , and DTPA). However, the carbonate (or bicarbonate) anion *per se* also appears to have a role in this system, which differentiates carbonate from caustic liquors in pulp brightening and bleaching systems. The fast decomposition of peroxide in carbonate liquor is suppressed by addition of high concentrations of magnesium, such that the addition of 400 ppm Mg^{2+} (313 K, pH = 10.3, ionic strength = 2.25M) reduces the estimated first-order rate constant for peroxide decomposition at 313 K from about $50 \text{ E-}5$ to $0.05 \text{ E-}5 \text{ s}^{-1}$.

INTRODUCTION

Hydrogen peroxide is used for brightening and bleaching wood pulp (1) in the presence of an alkali, which maintains the liquor pH around 10–11, where the perhydroxyl anion (HO_2^-) is available from dissociation of H_2O_2 ($\text{pK}_a = 11.7$ at 298 K). Sodium hydroxide (NaOH) is normally used to control pH, but other sources of alkali have been investigated (2, 3, 4, 5). Sodium carbonate (Na_2CO_3) is a candidate alkali source that is common in chemical pulp mills and is also available as the product of chemical recovery in closed-cycle chemimechanical pulp mills (6).

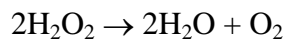
Depending on concentration and temperature, sodium carbonate/bicarbonate forms buffered aqueous solutions in the pH range 9–12. In this respect, Na_2CO_3 should be an ideal base for

peroxide brightening/bleaching. However, several studies of the replacement of NaOH by Na₂CO₃ have shown that carbonate liquors are not as effective as caustic liquors for peroxide brightening, particularly with high (2–4%) peroxide charges (2, 4, 5). Thus our observation that

peroxide is less stable in carbonate liquor than in caustic liquor may be of interest to operators and researchers in the pulp and paper industry.

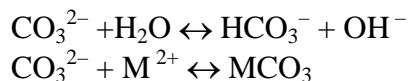
BACKGROUND

Hydrogen peroxide is an unstable compound whose decomposition is promoted by increasing pH and by the presence of catalytic metal ions, such as Mn, Fe, and Cu, in pulp and in process equipment (7, 8, 9, 10, 11). Peroxide decomposition is also catalyzed by the “heavy metals,” such as Pb, Ag, and Pt.



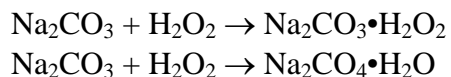
In bleaching or brightening pulp with peroxide, the standard practice is to use an alkaline liquor (10 < pH < 12), where the peroxide is stabilized by the addition of magnesium sulfate and sodium silicate, plus metal ion chelants such as DTPA. The alkaline condition is normally obtained by a charge of 1–4 wt.% NaOH on pulp.

One would anticipate that for a given pH and temperature, the rate of decomposition of peroxide in pulp liquors will not be affected by replacement of NaOH by Na₂CO₃. The carbonate anion is hydrolyzed in water to bicarbonate, decomposed to CO₂ by acids, and forms precipitates with many metal ions (such as Ca, Mg, Fe, Mn, Pb, etc.), but otherwise is not noted for its reactivity.



Any difference in peroxide stability between NaOH and Na₂CO₃ could be due to differences in the levels of catalytic impurities such as transition metal ions, which are known to contaminate sodium carbonate.

However, solid sodium carbonate does combine with hydrogen peroxide to form a carbonate peroxyhydrate, or perhaps peroxycarbonate (12, 13):



These products are not stable, but such reactions may influence the activity of peroxide in carbonate liquor. Previous workers (14) have shown that the decomposition of hydrogen peroxide in alkaline solutions (pH about 12, 303 K, ionic strength ca. 1–2M) is accelerated by the presence of carbon dioxide, and they have postulated the involvement of peroxycarbonate in the decomposition process. Others have shown that this effect of carbon dioxide disappears in

purified solutions, and they have invoked transition metal carbonato-complexes as catalysts for peroxide decomposition (13, 15). The presence of carbonate may also affect the free-radical mechanisms of peroxide decomposition (9, 10, 11), but there are no studies of this matter reported in the literature.

In our work on the electrosynthesis of hydrogen peroxide in strong sodium carbonate/bicarbonate solutions for mechanical pulp brightening, we encountered the anomalous rapid decomposition of peroxide in carbonate liquor. The studies described below were done to compare the stability of peroxide in caustic liquor vs. concentrated (0.1–1M) carbonate liquor and to examine the effects of peroxide-stabilizing additives on the decomposition of peroxide in carbonate liquor.

EXPERIMENTAL

Three sets of experiments were done to examine the stability of peroxide.

- To compare the rate of decomposition of hydrogen peroxide, without peroxide-stabilizing additives, in aqueous solutions of sodium hydroxide vs. sodium carbonate at the same pH, temperature, and ionic strength.
- To determine the effects of the conventional peroxide-stabilizing agents—magnesium sulfate, sodium silicate, and DTPA—on peroxide stability in sodium hydroxide vs. sodium carbonate liquor.
- To find the effect of several candidate peroxide-stabilizing agents on peroxide stability in sodium carbonate liquor.

In recognition that many factors affect the stability of peroxide in alkali, Set A(1) engaged four independent variables—source of base, temperature, pH, and ionic strength—in a two-level factorial experiment (16), with the rate of peroxide decomposition as the dependent variable.

The experiment of Set A(1) used the full factorial set ($2^4 = 16$ runs) plus midpoint replicates for a total of 20 runs, performed in random order. In each run, 750 mL of liquor was preheated to the reaction temperature in a glass beaker with a Teflon-coated stirrer. Reagent H_2O_2 (30 wt.%) was added for an initial peroxide concentration of about 0.1M, and the solution was sampled (2 mL) at intervals during 3-hour runs, then analyzed for peroxide by permanganate titration in acid (17). The presence of unaccounted peroxy carbonate species (if they existed) is discounted by the excess acid added prior to titration.

Liquors were prepared in distilled water by mixing reagent-grade Na_2CO_3 or NaOH with NaCl, for the required combinations of pH and ionic strength, with pH measured at the reaction temperature. The Na_2CO_3 concentration of the carbonate liquors ranged from 0.1 to 1M, while the NaOH in the caustic liquors ranged from 0.025 to 0.1M. Concentrations of NaCl required for adjustment of the ionic strength ranged from zero in 1M Na_2CO_3 to 2.975M in 0.025M NaOH. The pH of each reacting mixture was subsequently controlled during the run to ± 0.1 pH units by dropwise manual addition of 1M HCl, and temperature was controlled to ± 1 K by a water bath. In

addition, samples of each reagent were analyzed for trace metals at the ppm level, and these values were used to estimate the trace metal content of the liquors given in **Table I**.

To remove the effect of variations of transition metal content between the reagent grade hydroxide and carbonate liquors, a second set of runs at the *midpoint* conditions of Set A(1) (313 K, pH = 10.3, I = 2.25M) were subsequently done (with replicates) in hydroxide and carbonate solutions with nearly the same trace metal concentration. In these runs [Set A(2)], the hydroxide solution was prepared by adding 0.28 L of 10M hydrochloric acid to 1 L of 2.9M NaOH, while the carbonate solution was prepared by absorbing bottled CO₂ gas into the mixture obtained by adding 0.13 L of 10M hydrochloric acid to 1 L of 2.1M NaOH. The approximate trace metal content (expressed in units of ppm wt.) of the hydroxide and carbonate solutions was, respectively:

[0.03 Ag / <0.004 Cr / <0.004 Cu / 0.8 Fe / <0.008 Hg / <0.002 Mn / 0.018 Ni]

and

[0.02 Ag / <0.003 Cr / <0.003 Cu / 0.4 Fe / <0.006 Hg / <0.0015 Mn / 0.012 Ni]

Set B consisted of a two-level factorial experiment, with midpoint replicates, on the rate of peroxide decomposition, with the four independent variables shown in Table III. The solutions were prepared from reagent-grade chemicals, and peroxide concentrations were measured as described for the factorial runs of Set A(1).

Table I. Metal content of liquors for Set A(1) — without additives

pH		10		10.6	
Temperature, K		303	323	303	323
Source of base	Ionic strength, M	<i>Heavy metals / Fe / Mn, ppm wt.</i>			
Na ₂ CO ₃	1.5	0.40/0.19/<0.08	0.35/0.22/<0.07	0.27/0.27/<0.05	0.27/0.27/<0.05
	3.0	0.85/0.37/<0.17	0.79/0.40/<0.16	0.71/0.45/<0.14	0.53/0.53/<0.10
NaOH	1.5	0.44/0.18/<0.09	0.45/0.19/<0.09	0.45/0.19/<0.09	0.46/0.21/<0.09
	3.0	0.89/0.36/<0.18	0.90/0.37/<0.18	0.89/0.37/<0.18	0.90/0.38/<0.18

Set C used individual runs to measure the rate of peroxide decomposition in a reagent-grade sodium carbonate/bicarbonate solution, with additives selected for the potential to stabilize peroxide (Table IV).

RESULTS AND DISCUSSION

Tables II and III show the results from the factorial runs of Set A(1) and Set B, in terms of the first-order peroxide decomposition rate constant “k,” which was estimated by fitting the experimental data. **Figure 1** shows curves of Set A(2) for the decomposition of peroxide at 313 K, pH = 10.3, I = 2.25M, in caustic and in the corresponding carbonated solution with nearly the same concentration of trace metals.

Table II. Factorial results from Set A(1)
Rate of peroxide decomposition in caustic and carbonate liquors without additives

pH		10		10.6	
Temperature, K		303	323	303	323
Source of base	Ionic strength, M	First order H_2O_2 decomposition rate constant ($1 E-5 s^{-1}$)			
Na ₂ CO ₃	1.5	18	160	22	93
	3.0	11	78	14	93
NaOH	1.5	2	24	1	26
	3.0	2	10	2	18

From center-point replicates. Standard deviation of $k = 3 E-5 s^{-1}$; confidence interval of $k = 7 E-5 s^{-1}$.
Reagent-grade chemicals. No additives, except NaCl to fix ionic strength. Values of "k" rounded to nearest integer.

The most notable result of Table II is an average *ninefold increase* of peroxide decomposition rate on changing the source of base from NaOH to Na₂CO₃. Analysis of variance of the data of Table II shows that, at the 95% confidence level, both temperature and source of base have a significant positive effect on (i.e., increase) the rate of peroxide decomposition. Ionic strength has a significant negative effect on peroxide decomposition, and the effect of pH is not significant at the 95% level. The analysis also reveals a significant positive interaction between temperature and source of base, which implies that increasing temperature has a larger effect on peroxide decomposition rate in Na₂CO₃ than it does in NaOH. Other interactions are not significant at the 95% level. However, the data do show significant curvature, as may be expected from the effects of pH, temperature, and composition in a complex chemical system such as this.

The effect of changing the source of base is substantiated by Fig. 1, from which the first-order rate constants are $10 E-5 s^{-1}$ in hydroxide and $48 E-5 s^{-1}$ in carbonate solution of nearly the same trace metal concentration.

Table III. Factorial results from Set B
Rate of peroxide decomposition in caustic and carbonate liquors with additives

Na ₂ SiO ₃ , M		0		0.025	
Mg ²⁺ , ppm wt.		0	10	0	10
Source of base	Na ₄ DTPA, wt.%	First order H_2O_2 decomposition rate constant ($1 E-5 s^{-1}$)			
Na ₂ CO ₃	0.0	48.2	42.8	20.7	0.2
	0.3	2.5	2.7	3.5	3.0
NaOH	0.0	15.3	0.3	8.0	0.0
	0.3	1.8	1.7	1.8	2.2

From midpoint replicates. Standard deviation of $k = 4 E-5 s^{-1}$; confidence interval of $k = 8 E-5 s^{-1}$.
Temperature = 313 K, pH = 10.3, ionic strength = 2.25M. Reagent-grade chemicals.

Table III indicates the expected effects of the conventional stabilizing agents in suppressing peroxide decomposition in both caustic and carbonate liquors, plus an increase in decomposition rate when the source of base is changed from NaOH to Na₂CO₃. Analysis of variance shows that at the 95% significance level, both silicate (0–0.025M) and DTPA (0–0.3 wt.%) decreased the

rate of peroxide decomposition, while source of base (NaOH to Na₂CO₃) increased the rate of decomposition. Significant interactions were silicate/Mg, which decreased the rate, plus silicate/DTPA and DTPA/Mg, which increased the rate of peroxide decomposition. The curvature was not significant at the 95% level.

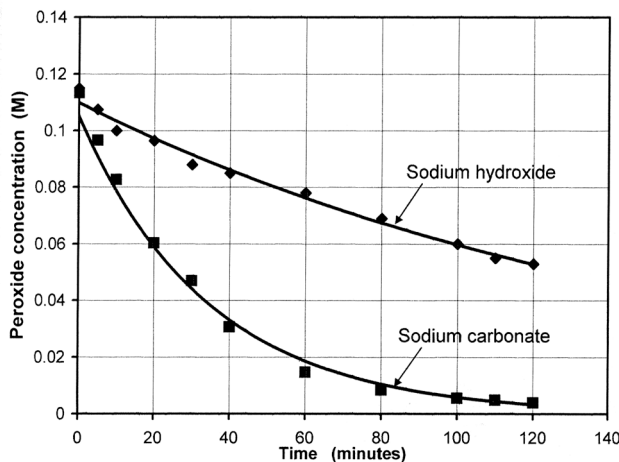


Figure 1. Decomposition of peroxide in caustic and in carbonate liquors of essentially the same trace metal content. (Experiment Set A(2), 313 K, pH = 10.3, I = 2.25M).

Some of the results of experiment Set C are given in **Table IV**. These data indicate that peroxide decomposition in carbonate liquor is suppressed by high levels of magnesium (ca. 100 ppm), while aluminum, calcium, and tin at 100 ppm have relatively little effect. The rate constant also dropped to about 2 E-5 and 7 E-5 s⁻¹, respectively, with DTPA and with phosphonate chelant at 0.3 wt.%, and to about 30 E-5 s⁻¹ with 100 ppm of sodium pyrophosphate, tripolyphosphate, tetraborate, or metaborate.

Table IV. Results for Set C

Effect of additives on rate of peroxide decomposition in carbonate liquor

Additive (ppm)	None	Mg(10)	Mg(100)	Mg(200)	Mg(400)	Al(100)	Ca(100)	Sn(100)
k, 1 E-5 s ⁻¹	48	42	5.7	0.7	0.05	26	29	22

k = peroxide decomposition rate constant; variance = 2 E-5 s⁻¹; all at 313 K, pH = 10.3, I = 2.25M (Na₂CO₃ + NaCl)

The results of Fig. 1, plus Tables II and III, show a strong effect of the source of base (NaOH or Na₂CO₃) on peroxide decomposition, although it is uncertain whether this effect is due to the presence of the carbonate anion *per se*, to trace metals that accompany the sodium carbonate, or to an interaction of these variables. The trace metal contents of the reagents used in experiments A(1), B, and C are different, and the metal components that are known peroxide decomposition catalysts (e.g., Mn, Fe, Cu, Ni, Cr, Ag, Hg, Pb) are not fully specified, since many are below the limit of detection in the trace metal analyses summarized in Table I.

However, from liquor compositions of Table I, it is unlikely that the large effect of Na₂CO₃ vs. NaOH in Tables II and III is due to the small variations in metal content in the liquors. This observation is reinforced by Fig. 1, which shows a fivefold increase of peroxide decomposition rate from hydroxide to carbonate liquors with nearly the same trace metal content. Based on these comparisons, it is our tentative conclusion that the presence of the carbonate (or bicarbonate) anion is responsible for the increased rate of peroxide decomposition in carbonate liquor. The mode of action of carbonate may be through the formation of transition metal carbonato-complexes (13, 15), which catalyze peroxide decomposition, or by interference in the metal-induced free-radical route (Fenton cycle) of peroxide decomposition (11).

The fact that conventional peroxide-stabilizing agents suppress peroxide decomposition in carbonate liquor implies the involvement of catalytic metal ions in the reaction. However, it seems from Tables III and IV that magnesium alone is less effective in carbonate liquor than in caustic liquor. This may result from the role of magnesium hydroxide and carbonate precipitates in the redox stabilization of transition metals (such as Fe and Mn) (18, 19), where the solubility products of Mg(OH)₂ and MgCO₃ are, respectively, about 9 E-12 and 4 E-5 at 298 K (20). Experimentally we noted that peroxide stabilization by magnesium in carbonate liquors matched the visual appearance of a white colloidal suspension, which occurred above about 100 ppm Mg²⁺. Such an effect may be due to interactions between the catalytic metals, Mg²⁺, OH⁻, and CO₃²⁻. In view of the conclusions of Liden and Ohman (18, 19), it seems more than coincidence that effective stabilization of peroxide by magnesium in 0.35M sodium carbonate at pH 10.3 is obtained when the ionic product [Mg²⁺][OH⁻]², in equilibrium with MgCO₃, nearly equals the solubility product of Mg(OH)₂.

CONCLUSIONS

Hydrogen peroxide decomposes about nine times faster in sodium carbonate liquor than in sodium hydroxide liquor. This observation is based on laboratory data obtained using aqueous solutions of reagent-grade chemicals at temperatures of 303–323 K, pH 10.0–10.6, and ionic strength 1.5–3.0M. Peroxide decomposition in the carbonate liquor is suppressed by the conventional alkaline peroxide-stabilizing agents (MgSO₄, Na₂SiO₃, and DTPA) and presumably is caused by the same catalytic metal ion (e.g., Fe, Mn) redox cycle as that documented for caustic liquors.

Magnesium alone is not as effective for peroxide stabilization in carbonate liquor as in caustic liquor, but peroxide decomposition in carbonate liquor is strongly suppressed by the addition of magnesium sulfate at Mg²⁺ levels of about 400 ppm. The mechanism may involve interactions between the catalytic metal ions, Mg²⁺, OH⁻, and CO₃²⁻ in the redox stabilization of transition metals by magnesium precipitates.

Our data corroborate the results of Csanyi *et al.* (14, 15) and indicate that the relatively low stability of peroxide in carbonate liquor is not due to extra metal contamination but, rather, to the interference of carbonate in the mechanism of peroxide decomposition by catalytic metal ions. These results imply that the carbonate (or bicarbonate) anion has a role in promoting peroxide

decomposition, which thus differentiates carbonate from caustic liquor in pulp brightening and bleaching systems.

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