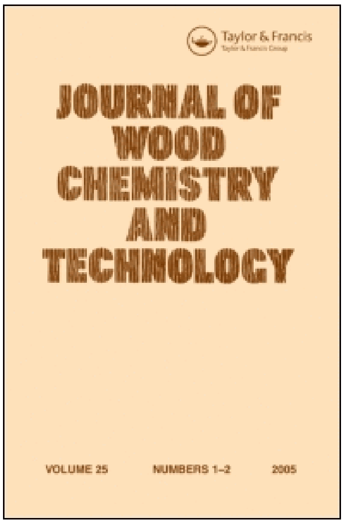

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Studies on Ozone Bleaching. I. The Effect of PH, Temperature, Buffer Systems and Heavy Metal-Ions on Stability of Ozone in Aqueous Solution

G. Y. Pan[ab]; C. -L. Chen[a]; H. -M. Chang[a]; J. S. Gratzl[a]
[a] Department of Wood and Paper Science, North Carolina State University, Raleigh, North Carolina, USA [b] International Paper Company, Tuxedo Park, New York

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STUDIES ON OZONE BLEACHING. I.
THE EFFECT OF PH, TEMPERATURE, BUFFER SYSTEMS AND HEAVY METAL-IONS ON STABILITY OF OZONE IN AQUEOUS SOLUTION*

G. Y. Pan**, C.-L. Chen, H.-m. Chang and J. S. Gratzl
Department of Wood and Paper Science
North Carolina State University
Raleigh, North Carolina 27695-8005, USA

ABSTRACT

Ozone was found to be reasonably stable at moderately low pH (∿ pH 3) and ambient temperature in acetic, sulfuric and nitric acid solutions. In these cases, the exact kinetic order of ozone decomposition could not be established. However, second order with respect to ozone was preferred on the basis of statistical analysis of the data. At pH 3, the ozone decomposition rate was found to be slightly higher at 15°C and moderately higher at 35°C than at 25°C for all three buffer systems. At lower concentration level (∿ 0.5 ppm), only Co(II) ion enhanced decomposition of ozone in sulfuric acid solution at pH 3 and 25°C. In contrast, at the higher concentration level (∿ 3.0 ppm), Ca(II), Cr(III), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) ions were found to contribute the decomposition of ozone; the effect of Co(II) and Fe(II) ions was very pronounced as compared to the other ions. Using acetic acid instead of sulfuric acid as buffer reagent resulted in drastic and moderate reductions of the ozone decomposition catalyzed by Co(II) and Fe(II) ions, respectively. These indicate that acetic acid acts as radical scavenger for hydroxyl radical as postulated by Walling et al. Thus, the drastic increase in the ozone decomposition in the sulfuric acid solution with the pre-

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* Dedicated to Professor Joseph L. McCarthy on his 70th birthday.

** Present Address: International Paper Company, Tuxedo Park, New York 10987

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sence of Co(II) or Fe(II) ion is caused by free radical chain reactions initiated by free radicals produced in the process.

INTRODUCTION

Increasing concern about the environment in the past decades has led to the development of less polluting alternatives in pulp bleaching processes. Research has primarily been focused on substituting, partially or totally, chlorine and chlorine-based chemicals with oxygen and oxygen-based compounds, such as ozone and hydrogen peroxide.

Ozone was suggested for bleaching of wood pulp as early as 1871[1] but high production costs, excessive consumption and frequent uncontrollable losses in pulp strength have so far prevented its application on a larger scale. One of the major impediments to its use as a bleaching agent is obviously its moderate stability in aqueous solutions. Ozone is a rather strong and highly specific oxidant. It has, however, a tendency to decompose in water, generating, among others, some very reactive, highly unselective oxidizing species.

The chemical interactions between ozone and water are established in numerous kinetic studies on ozone decomposition and in studies on the oxygen exchange rate. The investigations cover practically the entire pH range at temperatures between 0-60°C. The decay is catalyzed by base (^-OH) and is expressed in the following general rate expression:

$$- d[O_3]/dt = k \cdot [O_3]^a \cdot [^-OH]^b$$

The reaction order "b" with respect to hydroxide ion concentration varies from 0.36-1.00[2-6] and "a" for ozone is 1, 1.5 or 2.0[2,3,7,8], depending on the pH. However, there are great discrepancies among rate constants and reaction orders reported in the literature. The major causes for discrepancies have been attributed to the presence of impurities[7], differences in analytical procedures[3] and failure to apply statistical methods in analyzing experimental data[8].

Although there is no agreement as to the initiating step, both hydroxyl and perhydroxyl radicals have been generally accepted as chain carriers in this process [2,3,9]. Further support of radical reaction patterns was provided by tracer studies[10]. Recently, Hoigne et al [11-13], were able to show that hydroxyl radicals are generated in the hydroxide ion catalyzed decomposition, and that about 0.5 mole of hydroxyl radicals are produced per mole of ozone at pH 10.5.

The objectives of the present work were twofold: (a) to establish reliable kinetics on the decomposition of ozone in aqueous solution and the effects of transition metal-ions and radical scavengers on the reaction, and (b) to elucidate possible mechanism for these reactions. Fundamental information on ozone-carbohydrate and on ozone-lignin reactions, especially in aqueous medium, is rather limited. Moreover, many discrepancies and confusion still exist at the present on the kinetics of ozone decomposition in water. It is, therefore, necessary to first establish our own basic data for the kinetics of the ozone-water system before embarking on investigations of ozone-carbohydrate reactions.

RESULTS AND DISCUSSION

Effect of pH and Buffer Systems

The experiments were conducted with double distilled water and restricted to the pH range from 2-7 and temperatures from 15-35°C. Multiple runs were performed at each pH level to generate reliable and reproducible kinetic data and whenever suitable, the data were subjected to statistical analysis. The bulk of the data was collected from runs at 25°C, as compiled in Tables 1 and 2 and

TABLE 1. Rate Constants of Ozone Decomposition at Various pH at 25°C With Ozone Decomposition Monitored up to 80% Completion.

Buffer System	pH	No. of runs	Average k 1 1/2 order $mole^{-1}$ ℓ min^{-1}	Average k 2nd order $mole^{-1/2}$ ℓ $^{1/2}$ min^{-1}	Preferred reaction order
KH_2PO_4 + NaOH	7	4	0.83 ± 0.03	143 ± 8	2nd order
KH_2PO_4 + NaOH	6	4	0.71 ± 0.02	111 ± 2	2nd order
AcOH + AcONa	5	2	0.24 ± 0.00	34 ± 2	1 1/2 order
HNO_3	5	1	0.27	42	1st order $k_{1.0}$ = 0.007
H_2SO_4	3.5	1	0.09	12	2nd order
HNO_3	3.5	2	0.09 ± 0.00	12 ± 0	2nd order
AcOH	3.5	3	0.04 ± 0.00	6 ± 0	2nd order
AcOH + NaAC	3	3	0.11 ± 0.00	15 ± 1	1 1/2 order
HNO_3	2	3	0.05 ± 0.00	7 ± 0	2nd order

NOTE:

(1) Ozone solutions of various buffer systems were prepared by ozonization for one hour.

(2) An extinction coefficient, ξ = 2334 ℓ $mole^{-1}$ cm^{-1}, was used in the calculation of rate constants.

TABLE 2. Rate Constants of Ozone Decomposition at Various pH at 25°C With Ozone Decomposition Monitored up to 100 Minutes.

Buffer System	pH	No. of runs	Average k 1 1/2 order $mole^{-1/2}\ \ell^{1/2}\ min^{-1}$	Average k 2nd order $mole^{-1}\ \ell\ min^{-1}$	Preferred reaction order
KH_2PO_4 + NaOH	7	4	0.83 ± 0.03	143 ± 8	2nd order
KH_2PO_4 + NaOH	6	4	0.70 ± 0.02	111 ± 2	2nd order
AcOH + AcONa	5	2	0.24 ± 0.01	30 ± 0	equally preferred
HNO_3	5	1	0.22	28	1st order $k_{1.0} = 0.007$
H_2SO_4	3.5	1	0.16	16	2nd order
HNO_3	3.5	2	0.13 ± 0.00	15 ± 1	2nd order
AcOH	3.5	3	0.11 ± 0.01	11 ± 1	2nd order
AcOH + AcONa	3	3	0.09 ± 0.02	10 ± 3	2nd order
HNO_3	2	3	0.06 ± 0.00	6 ± 0	1st order $K_{1.0} = 0.002 \pm 0.0005$

REMARKS

(1) Ozone solutions of various buffer systems were prepared by ozonization for one hour.

(2) An extinction coefficient, $\xi = 2334\ \ell\ mole^{-1}\ cm^{-1}$, was used in the calculation of rate constants.

illustrated in Figure 1. A detailed analysis of the data revealed that the decomposition reactions were either first, first and a half or second order with respect to ozone concentration. Since in most of the cases we were not able to establish clearly the reaction order, we have indicated our preference based on the best data fit. There were, for instance, also cases where the data fit two kinetic orders equally well. Difficulties in defining the exact kinetic order have been repeatedly reported[2,6,8].

The rate constants listed in Table 1 were computed from data obtained from experiments carried out to 80 percent completion. This was achieved in about 100 minutes in runs of pH 6-7, while at lower pH levels (around pH 3), it required about 600 minutes. As expected, rate constants obtained from short-time experiments up to 100 minutes (Table 2) differed somewhat from those obtained from long-time experiments (Table 1). Closer inspection of the rate data in Table 1 and Table 2 indicates that buffer systems do have some effect on ozone decomposition. Comparing, for instance, the acetic, sulfuric and nitric acid buffer systems at pH 3.5 shows that the acetic acid buffer is superior to the other two in stabilizing ozone. For the decomposition of ozone in acetic acid solution at pH 3.5 and 25°C, a second order rate constant is determined to be 6 $\text{mole}^{-1}\ \ell\ \text{min}^{-1}$ which is 50% smaller than those obtained in the other two acid solutions under the same conditions. Cautions should be taken, however, in using the data obtained in the acetic acid buffer system because (a) the data fit to the second order kinetics in this case is not as good as those in the other two systems and (b) the rate data tend to reflect more of those data points taken in the later phase of the reaction when the decomposition rate in the acetic acid system becomes much lower than those in the other two systems. A plot of ozone concentration versus time for the first 70 minutes of reaction in sulfuric and acetic acid solutions at pH 3 reveals that the difference in the decomposition rate is actually small at 15 and

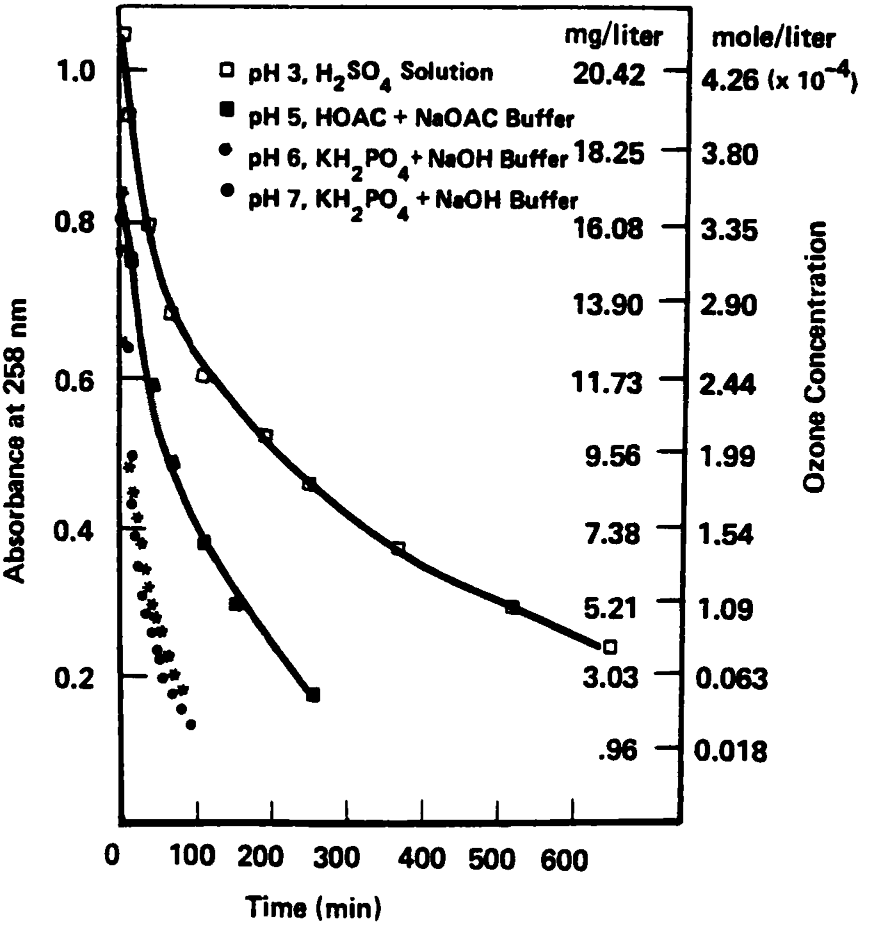


Figure 1. Effect of pH on Ozone Decomposition at 25°C.

25°C (Figure 4 reference curves). Only at 35°C does a noticeable difference exist. On the other hand, when the data fit is good as those in the H_2SO_4 and HNO_3 buffer systems, the agreement of rate constants is excellent. The rate constants at pH 5 in acetate buffer system and in nitric acid solution is also close. The pH dependence is summarized in Figure 2 where the rate constants are plotted versus pH, showing a rapid increase from pH 4 to 7.

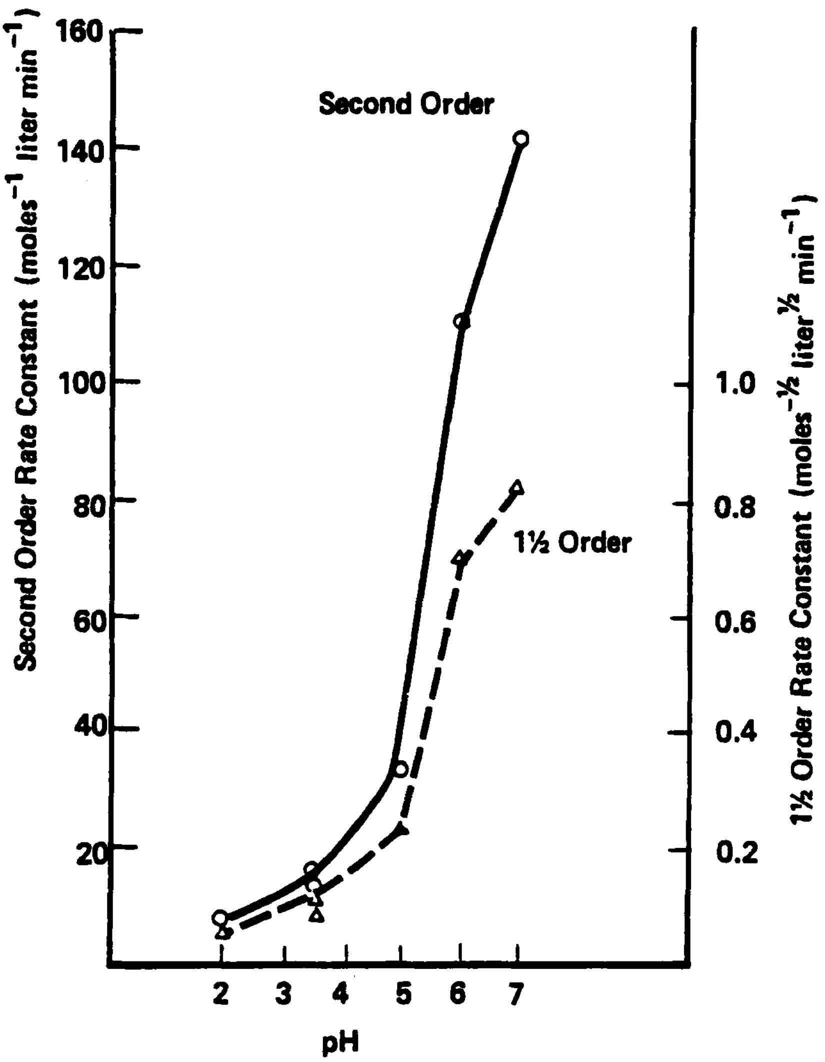


Figure 2. Effect of pH on Ozone Decomposition at 25^0.

Effect of Repeated Ozonization

The economic feasibility of low or medium consistency ozone bleaching in the future may very well to a large extent depend on the possibility of recycling the bleach effluents. The problem one can anticipate is that in the course of ozone decomposition, radical species are generated which in turn accelerate the decay of ozone, resulting in excessive ozone consumption. On the other hand, the radical species react not only with organic material but also with inorganics as well. It is, therefore, conceivable that repeated use of the effluents could result in different, presumably enhanced, decomposition rates in each of the subsequent ozonization stages. Accordingly, experiments were designed to simulate such systems. Several runs were conducted at pH 3 and 5 using appropriate acetate buffer or sulfuric acid for pH-adjustment. Since ozone concentration was monitored in each run from about six hours and the time elapsed between ozonizations was 12 hours (overnight), the reaction was actually being followed for a period of several days (Table 3).

While at pH 5 the decomposition rate increased by a factor of 7 between the first and the fourth steps to a level as high as that observed in single runs carried out at pH 7, only a two-fold increase was noticed at the fourth step at pH 3, amounting to only about a fourth of the rate of the above reference. Experiments on shorter ozonizations (10 minutes) and shorter periods between treatments (6 hours) conducted in sulfuric acid solution at pH 3 showed that in this case there was no change in the decomposition rates as a result of repeated ozonization.

Effects of Heavy Metal-Ions and Temperature

The experiments were conducted in sulfuric acid solution at pH 3 (sulfuric acid) and room temperature at two levels of metal-ion concentration, namely with about 0.5 ppm (0.009 mM) and about

TABLE 3. The Effect of Repeated Ozonization on Rate Constants

System	pH	Ozonization Step*	1 1/2 order rate constant $(mole^{-1/2}\ \ell^{1/2}\ min^{-1})$	2nd order rate constant $(mole^{-1}\ \ell\ min^{-1})$
AcOH + AcONa	5	1st	0.23	32
		2nd	0.46	71
		3rd	0.85	136
		4th	1.54	323
H_2SO_4	3	1st	0.09	12
		2nd	0.16	23
		3rd	0.17	24
		4th	0.21	32
HNO_3	3	1st	0.09	12
		2nd	0.13	19
		3rd	0.15	23

* The buffer solutions were ozonized for 60 minutes in each step before the decomposition of ozone was traced.

3.0 ppm (0.05 mM) solutions. Except for copper ions (Cu^{++}) all the other metal ions were in the lower oxidation state such as Fe^{++}, Co^{++}, Ni^{++} and Cr^{+++}. In all cases, we used the metal sulfates to avoid possible complications caused by different anions. We also included Ca^{++}, which were added in form of calcium nitrate for reasons of solubility.

At the lower level (∿ 0.5 ppm) only Co^{++} enhanced decomposition of ozone. At the higher level (∿ 3 ppm) all species (except Ni^{++}) investigated contributed to the decomposition of ozone as shown in Figure 3. It was found that the ozone consumption was substantially higher than the amount required for oxidizing the metal ions to the higher valence state suggesting the involvement of chain reaction. The transition metal ion induced decomposition was very pronounced in the presence of Co^{++} and Fe^{++} as compared to the other species investigated.

Using acetic acid instead of sulfuric or nitric acid for pH adjustment resulted in drastic reduction in ozone decomposition

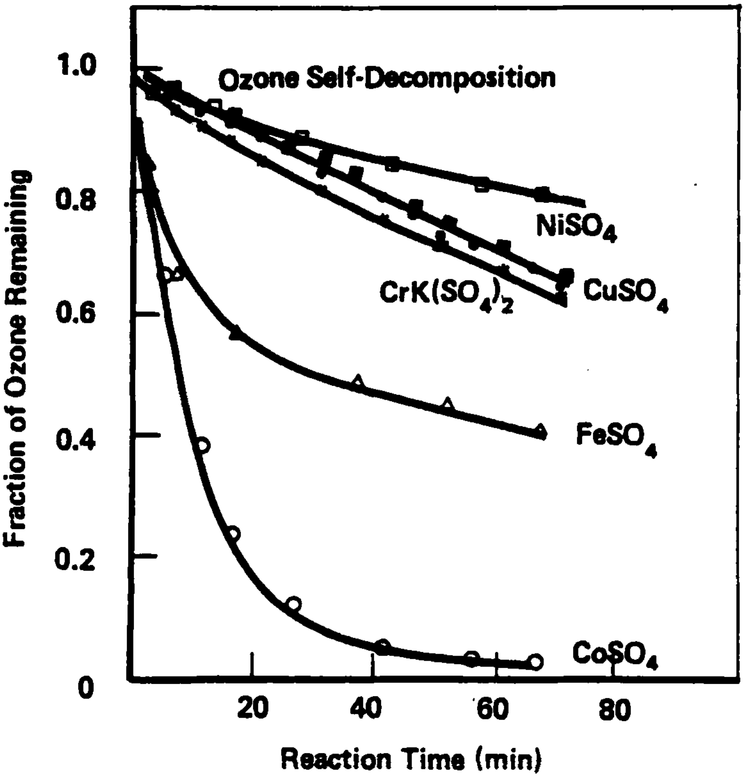
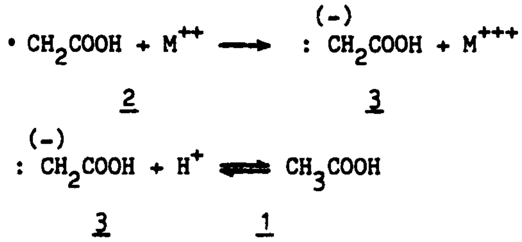


Figure 3. Effect of Metal-ions on Ozone Decomposition. O_3 : 0.4 mM; Metal-Ions: 0.05 mM; pH 3 (H_2SO_4); T = 25°C.

catalyzed by transition metal-ions. In the absence of metal ions, acetic acid caused only slight improvements in ozone stability. These observations can be rationalized in terms of reaction sequences proposed by Walling et al[14] shown in the following scheme:

$$\underset{\underline{1}}{CH_3COOH} + HO\bullet \longrightarrow \underset{\underline{2}}{\bullet CH_2COOH} + H_2O$$



$$\underset{\underline{2}}{\cdot CH_2COOH} + M^{++} \longrightarrow \underset{\underline{3}}{\overset{(-)}{:}CH_2COOH} + M^{+++}$$

$$\underset{\underline{3}}{\overset{(-)}{:}CH_2COOH} + H^{+} \rightleftharpoons \underset{\underline{1}}{CH_3COOH}$$

Acetic acid 1 acts actually as radical scavenger for hydroxyl radicals generated by metal induced decomposition of hydroperoxides or ozone and is oxidized to radical 2. Interaction between M^{++} and reduction of 2 to the carbanion 3, which is then protonated to the acid 1.

Studies on the temperature dependence of pH 3 solutions using various acids for pH adjustment revealed that at lower temperatures the stability was influenced little or not at all by the acids, with a significant difference noticed only at 35°C. The presence of Co^{++} resulted in a drastic enhancement of ozone decomposition, particularly in sulfuric acid solutions. In acetic acid solution, the Co^{++}-induced decomposition of ozone was significantly suppressed (Figure 4). The cobaltous ion catalyzed decomposition of ozone in sulfuric acid solution at pH 3 can be rationalized by the following reaction scheme proposed by Hill[15].

$$Co^{++} + O_3 + H_2O \longrightarrow Co(OH)^{++} + O_2 + HO\cdot$$

$$HO\cdot + O_3 \longrightarrow HO_2^{\cdot} + O_2$$

$$HO_2^{\cdot} + Co(OH)^{++} \longrightarrow Co^{++} + H_2O + O_2$$

By oxidizing Co^{++} to cobaltic hydroxide ion, $Co(OH)^{++}$, ozone decomposes to oxygen and hydroxyl radical (HO•), which in turn is oxidized by ozone to the perhydroxyl radical (HOO•). The Co^{+++} is reduced to Co^{++} by HOO•, which is oxidized to oxygen. The net result is the reduction of ozone to oxygen and the regeneration of the cobaltous ion (Co^{++}), which can initiate another cycle of

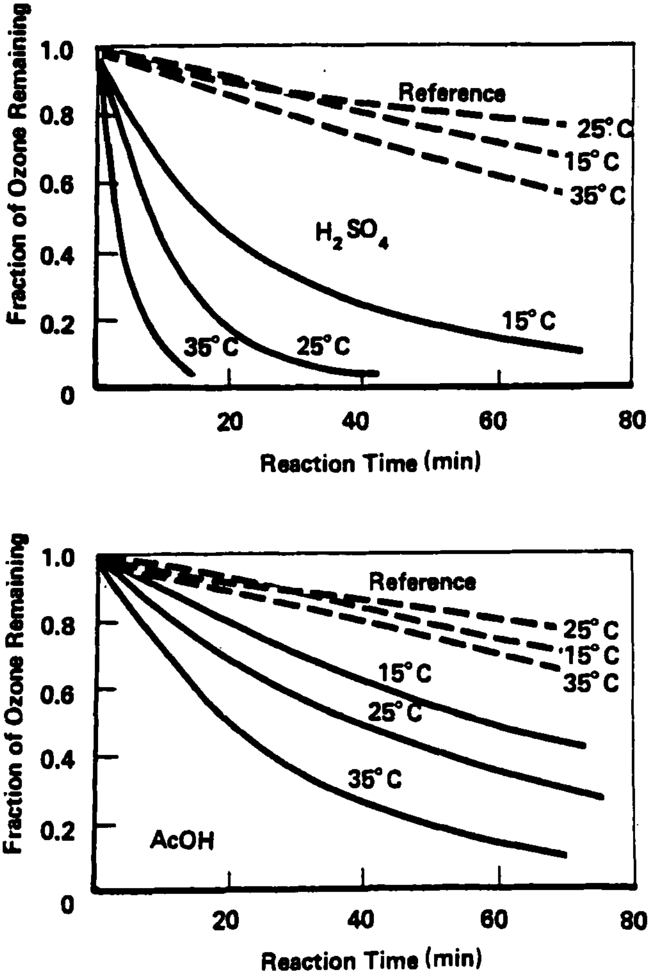


Figure 4. Effect of Co^{2+} on Ozone Decomposition at Various Temperatures.
O_3 : 0.4 mM; $CoSO_4 \cdot 7H_2O$: 0.05 mM; pH 3 (Upper: H_2SO_4; Lower: AcOH).

ozone decomposition reactions. In the presence of acetic acid, however, the following equilibrium between cobaltic hydroxide and the corresponding acetate exists:

$$Co(OH)^{++} + AcOH \rightleftharpoons Co(OAc)^{++} + H_2O$$

The equilibrium constant is estimated to be 4×10^3 indicating that the cobaltic acetate is the predominant species in the system. The latter is assumed to be reduced more slowly by perhydroxyl radical than the hydroxide complex, which seems to be the reason for the observed stabilizing effect of acetic acid. The decomposition of ozone in the presence of 0.05 mM cobaltous ion was found to fit the first order kinetics very well. When the logarithm of rate constants at various temperatures was plotted against the reciprocal absolute temperature, a straight line was obtained. The activation energy for the cobalt catalyzed decomposition of ozone was calculated to be 64 kJ/mole and 55.2 kJ/mole for the reactions in sulfuric acid and acetic acid solutions at pH 3, respectively. It is interesting to note that the slowdown of the cobaltous ion catalyzed decomposition by acetic acid is not the result of an increase in activation energy, but rather via a decrease in collision factor.

The presence of Fe^{++}, on the other hand, gives rise to a very moderate enhancement only, even in sulfuric acid solutions. Using acetic acid instead of sulfuric acid for pH-adjustment caused only a slight improvement in ozone stability (Figure 5). The curves in this figure have taken into account the absorption of ferric ion at λ 258 nm where the ozone concentration was measured. It was, therefore, necessary to establish an absorbance-concentration calibration curve for ferric ion using ferric nitrate solutions. Calculation using a second order rate constant of 1.7×10^5 l mole^{-1} sec^{-1} at 25°C[16] for $O_3 + 2Fe^{++} + 2H^+ \longrightarrow O_2 + 2Fe^{+++} + H_2O$ indicated that, under the experimental conditions, practically

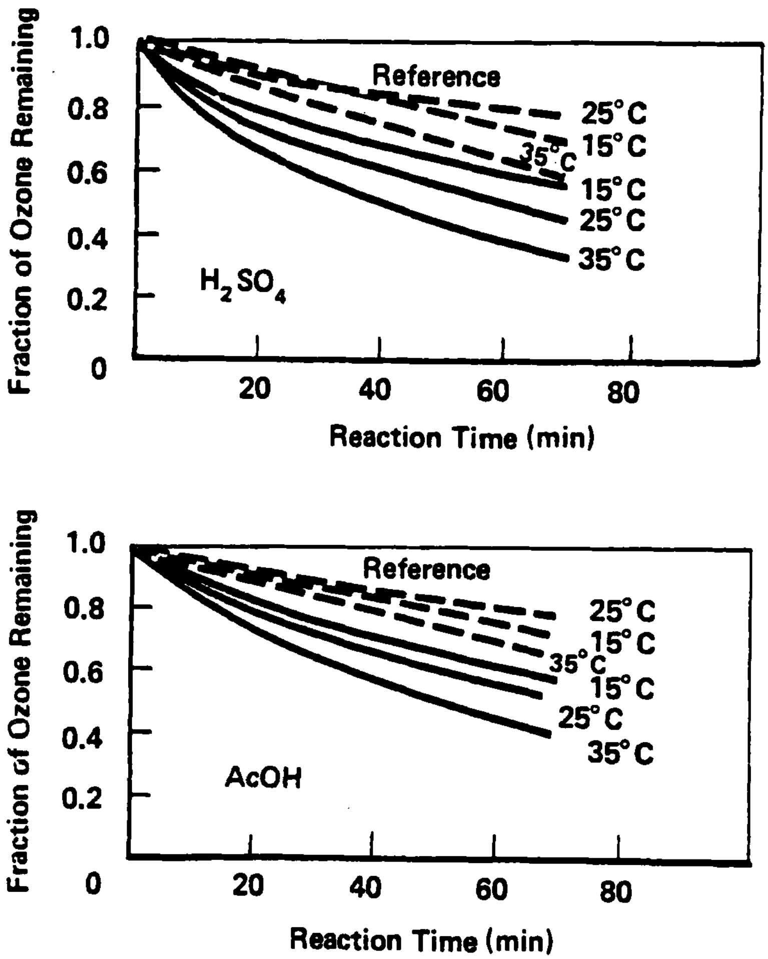


Figure 5. Effect of Fe^{2+} on Ozone Decomposition at Various Temperatures.
O_3 : 0.4 mM; $FeSO_4 \cdot 7H_2O$ = 0.05 mM; pH 3 (Upper: H_2SO_4; Lower: AcOH).

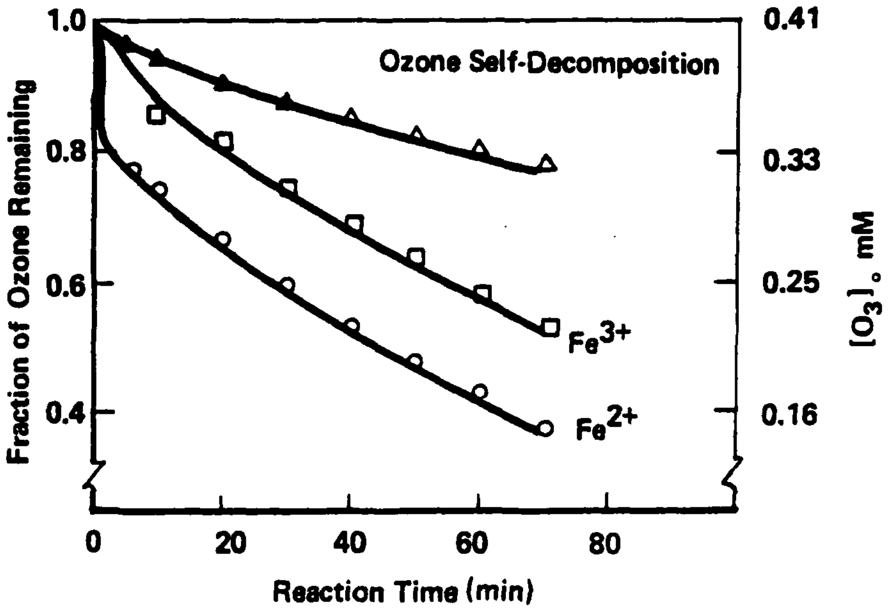


Figure 6. Effect of Fe^{2+} and Fe^{3+} on Ozone Decomposition. O_3 = 0.4 mM; $Fe^{2+(3+)}$: 0.05 mM; pH 3 (H_2SO_4); T = 25°C.

all of the ferrous ions were converted to ferric ions in less than 1 minute. It can therefore be expected that immediately after the reaction starts (within 1 minute), the ozone decomposition curve in the presence of ferrous ion will be parallel to that of the ferric ion catalyzed decomposition of ozone. As shown in Figure 6, this indeed is the case for the reaction in sulfuric acid solution at pH 3 and 25°C. The small but definite catalytic effect of the ferric ion suggests that perhydroxyl radicals are generated and are reacting with ferric ion, possibly via $Fe^{+++} + HO_2\cdot \longrightarrow Fe^{++} + H^+ + O_2$. The ferrous ion regenerated can then react with ozone, thus starting another decomposition cycle.

As mentioned previously, $HO_2\cdot$ and $HO\cdot$ had been postulated to act as chain carriers in the radical reactions involved in the decomposition of ozone in aqueous solution. The somewhat smaller catalytic effect of ferrous-ferric ions as compared to that of cobaltous-cobaltic ions can be explained in terms of the cobaltous-cobaltic catalyzed decomposition mechanism discussed above. Ferric ions and ferric hydroxide complexes are expected to be more stable than corresponding cobaltic ions and cobaltic complexes and thus, are less easily reduced to ferrous ions by perhydroxyl radicals. This is obviously due to the much lower oxidation potential of the ferric ion (0.77 volt) as compared to that of cobaltic ion (1.84 volts)[17]. As a result, the ferrous ion catalyzed decomposition reaction of ozone is much slower than that catalyzed by cobaltous ion.

Both temperature and type of acid used for pH adjustment have some effect on the ferrous ion catalyzed decomposition of ozone, but not as pronounced as observed in cobaltous ion catalyzed decomposition. The smaller temperature effect in the early stage of reaction suggests a rapid reaction between ozone and ferrous ion (i.e. low activation energy), whereas the small temperature effect in the later stage of reaction indicates that the concentration of perhydroxyl radicals and/or its reaction with ferric ion are not very temperature dependent. The smaller effect caused by differences in acids used for pH adjustment may be due to the much smaller equilibrium constant of $Fe(OH)^{++} + AcOH \rightleftharpoons Fe(OAc)^{++} + HOH$ reaction, $1.0 \times 10^{-7.7}$, as compared to 4×10^{3} for $Co(OH)^{++} + AcOH \rightleftharpoons Co(OAc)^{++} + HOH$. The $Fe(OH)^{++}$ ion is therefore the predominant species. As a result, the effect of acetic acid on the ferrous-ferric ion catalyzed decomposition of ozone is small. The equilibrium constant for first reaction was calculated from data presented in the literature [18,19].

CONCLUDING REMARKS

The present investigation on the kinetics of ozone decomposition in various aqueous solutions shows that ozone is rather sensitive to pH but not as sensitive to temperature and acids used for pH adjustment in the absence of both organic and inorganic substrates. Thus, ozone is reasonably stable in acetic acid, sulfuric acid and nitric acid solutions at pH around 3 and room temperature. The acetic acid buffer system is more effective than the other two acid buffer systems in stabilizing ozone.

In sulfuric acid solution at pH 3, Co^{++} is shown to be the most harmful chemical species to the stability of ozone at room temperature, followed by Fe^{++} and Fe^{+++}. The Co^{++} ion enhances decomposition of ozone even at the concentration level of 0.009 mM ($\sim$ 0.5 ppm). Using acetic acid solution at pH 3 instead of the sulfuric acid solution results in drastic and moderate reductions in the decomposition of ozone catalyzed by Co^{++} and Fe^{++}, respectively, at the concentration level of 0.05 mM ($\sim$ 3.0 ppm). These indicate that acetic acid acts as radical scavenger for hydroxyl radicals according to the reaction sequence postulated by Walling et al[14]. Thus, the drastic increase in the decomposition of ozone in the sulfuric acid solution with the presence of Co^{++} or Fe^{++} is probably caused by free radical chain reactions initiated by free radicals produced in the process. All of these imply that in mill operations, bleaching of pulp with ozone in aqueous solution would involve both free radical and ionic reactions. The free radical reactions would be predominant over the ionic reactions when transition metal-ions are present even in trace amounts in the water used in mill operations. This would have pernicious effect on both ozone consumption and pulp quality.

EXPERIMENTAL

Apparatus

Bulk oxygen (USP-grade) was passed through a moisture trap kept at - 80°C before entering the ozonator (Welsbach Model T-816). The saturated ozone solutions were prepared by bubbling an ozone-oxygen stream containing 60-80 mg ozone per liter at a flow rate of 1 liter per minute through the solutions in an absorbing vessel immersed in a temperature controlled ($\sim 0.1^{\circ}C$) water bath.

To avoid possible interference by traces of organic and inorganic impurities tap water was first distilled before deionization followed by a second distillation. The thus purified water had a very low heavy metal content (~ 0.2 ppm) and a conductivity of 0.495×10^{-6} mhos as compared to 0.138×10^{-3} mhos for tap water (heavy metal content ~ 2.0 ppm). All containers and tubings of the experimental setup were either glass or tygon.

Ozone-Concentration-UV-Absorbance at 258 nm Calibration

Ozone solutions of various concentrations were prepared by passing ozone through double distilled water (ddw) at temperatures ranging from 2-15°C and by diluting with ddw kept at the same temperature. Immediately after withdrawing an aliquot for UV-measurements a sample was analyzed iodometrically. A linear relationship was observed up to a content of 35 mg/ℓ. Applying the Statistical Analysis System (SAS) developed at North Carolina State University, the following linear regression equation, correlating absorbance A and concentration C, was computed.

$$A = 0.048\ C\ (\mathrm{mg}/\ell) = 2.333\ C\ (\mathrm{mM}/\ell) \quad (R^2 = 0.99)$$

From this equation, an absorptivity of 2334 $\ell\ \mathrm{mole}^{-1}\ \mathrm{cm}^{-1}$ was obtained and used for determining the rate constants of ozone consumption. The UV-measurements were carried out in Cary 15 or Pye Unicam SP8-100 spectrophotometers equipped with temperature controlled sample holders.

Ozone Stability

For several runs the pH of the solution was adjusted by appropriate buffer systems, such as acetic acid-sodium acetate for pH 3, and potassium dihydrophosphate-sodium hydroxide for pH 5, 6 and 7 solutions. To avoid possible interference by the ions of buffer systems,.the bulk of the kinetic runs were conducted with pH 3 solutions adjusted with sulfuric or acetic acid.At this pH, ozone was found to be reasonably stable.

The ozone/oxygen stream was not allowed to pass through the absorber before a constant ozone-content was achieved, which was accomplished after 5 to 10 minutes. Ozonization of solutions were carried out for 10 or 60 minutes, then an aliquot was transferred to a thermostated UV-cell. The absorbance at λ 258 mm was recorded in 5 to 10 minute intervals.

Runs in the presence of heavy metal ions were carried out exclusively in pH 3 solutions, adjusted either by acetic or sulfuric acid addition. The desired concentrations of metal ions were achieved by adding a few ml of a stock solution to several hundred ml of ozone solution under vigorous stirring. Timing was started when half of the volume was added. Immediately after addition was completed, a sample was taken for spectrophotometric determination.

In order to study the effect of metal ions unobscured by the possible interference by anions, the metal salts were added in form of their sulfates.

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