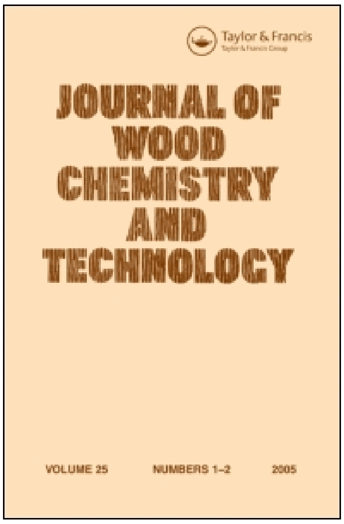


Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

The Chemistry of Ozone During Pulp Bleaching

Johan Lind[a]; Gabor Merényi[a]; Karin Wegner[b]
[a] Department of Chemistry, Nuclear Chemistry Royal Institute of Technology, Stockholm, Sweden [b] Swedish Pulp and Paper Research Institute, Stockholm, Sweden

To cite this Article Lind, Johan , Merényi, Gabor and Wegner, Karin(1997) 'The Chemistry of Ozone During Pulp Bleaching', Journal of Wood Chemistry and Technology, 17: 3, 297 — 326

To link to this Article: DOI: 10.1080/02773819708003133

URL: http://dx.doi.org/10.1080/02773819708003133

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 17(3), 297-326 (1997)

THE CHEMISTRY OF OZONE DURING PULP BLEACHING

Johan Lind and Gabor Merényi
Department of Chemistry, Nuclear Chemistry
Royal Institute of Technology
100 44 Stockholm, Sweden

Karin Wegner
Swedish Pulp and Paper Research Institute
114 86 Stockholm, Sweden

ABSTRACT

Using competition kinetics in the presence of various OH• radical scavengers, viscosity losses in ozonized pulp were shown to be caused by the cellulose reacting with both OH• radicals and ozone. The source of the OH• radicals was concluded to be the reaction between ozone and lignin, where OH• formation was ~0.5-3%. In the presence of ozone and oxygen, a chain reaction occurs in which OH•, O_2^{-}•, and cellulose-based radicals all function as chain carriers. At kappa numbers >2, the cellulose was degraded almost exclusively by OH• radicals. At the final kappa number of 2, ~50% of the viscosity loss was from direct attack of ozone on the cellulose.

INTRODUCTION

Ozone is a demonstrably powerful bleaching agent with excellent delignification properties. However, ozone is a very strong oxidant and does not possess the same selectivity towards lignin relative to cellulose as do chlorine-based chemicals, e.g., chlorine and chlorine dioxide. The prevalent view, supported by some experiments,[1] attributes this lack of selectivity to the generation, during ozone bleaching, of highly reactive and non-selective hydroxyl radicals.

In their ozonation studies of 1,2 dimethoxy benzenes in methanol, Eriksson and Gierer[2] detected muconic acid methylesters, formed as a result of ring opening along the 1-2 bond. Virtually no other products were detected. Lindholm[3] has shown that ozonation of pulp in water at pH 3 yielded ~0.3 carboxylic functions for every ozone molecule consumed. If the carboxylic functions are ascribed to muconic acid, these results indicate that only about 15% of the ozone consumed brings about aromatic degradation.

A further study of interest is one of ozonation of β-aryl ether model compounds.[5] The main products identified were derived from the fission of the ether linkage, rather than from aromatic ring opening. Unfortunately, only about 30% of the total products were recovered, the rest were apparently polymerized species. Judging by the absence of certain products, the same study also disclosed substantial amounts of radicals being produced subsequent to ozone attack on the β-aryl ether linkage.

Two major studies on the effect of transition metal ions during ozonation of high consistency (40%) pulp (HC) have been conducted. Colodette, et al.[5] subjected the pulp to pretreatment with complexing agents. Initially, their pulp contained 12.8 ppm Fe, 2.2 ppm Cu, and 71.9 ppm Mn. Upon reducing these values to 2.8 ppm Fe and < 1 ppm each of Cu and Mn at pH 6, the authors observed an increase of selectivity, defined as kappa drop(%)/viscosity drop(%), by a factor of 2.5. However, a similar pretreatment at pH 2 merely resulted in a 10% increase of the bleaching selectivity. A recent study[6] investigated the effect of added metal ions during ozonolysis of fully bleached pulp. With no lignin present to consume most of the ozone, the effect of deleterious metals on cellulose was maximized. At a constant ozone charge the viscosity loss in an essentially metal-free sample was found to be 22.5%. Upon addition of 100 ppm Fe^{+3} or Cu^{+2} to the sample the corresponding viscosity losses were no more than 29 and 33%, respectively. The above findings clearly reveal that, under HC conditions, metal ion-mediated ozone radical production is not critical at low pH. In contrast to the HC case, under low consistency (LC, 3%) conditions metal ions were found to affect the selectivity.[7]

Ozone Selectivity Estimated from Models

In model studies the selectivity, S, may be defined as $S = k_l/k_c$, where k_l and k_c are the rate constants of O_3 reacting with lignin and cellulose, respectively. By combining the relative rates reported by Eriksson and Gierer[8] and Kaneko et al.[9] with the absolute rate constant for creosol,[10] k_l is estimated to be 1500 $M^{-1}s^{-1}$ for an average aromatic lignin unit. For the reactivity of cellulose we take the literature value for glucose[11] which is 0.45 $M^{-1}s^{-1}$. Thus, S_{ozone} is predicted to be ≈3000. Assuming homogeneous conditions inside the fibre, the fraction of ozone reacting with cellulose, $O_3(C)$, is described by

$$O_3(C) = k_c[\text{Cellulose}] /(k_c[\text{Cellulose}]+kl[\text{Lignin}]) \qquad [1]$$

Utilizing the conversion factor of 0.152% lignin per kappa unit (note that weight percentages are about the same as mol% per monomer unit), Equation 1 is transformed into Equation 2.

$$O_3(C) \approx 1/(1 + 5 \text{ x kappa}) \qquad [2]$$

Recent studies indicate that lignin destruction occurs along a front.[12] Therefore, at low kappa numbers, ozone has to diffuse through parts of the fiber which have already been depleted of lignin. However, Equation 2 should be a fair approximation.

Radical Reactions of Cellulose in the Presence of O_3/O_2

As the present work will unequivocally demonstrate the production of hydroxyl radicals during ozonation of pulp, it is vital that the various modes of interaction of OH• with pulp be enumerated. Given that the ratio cellulose/lignin >70 and the selectivity of OH•, $S_{OH\bullet} \approx 7$ (the latter having been estimated from rate constants of OH• reacting with aromatics and sugars[13]), the majority of the OH• will react with cellulose. This will occur by abstraction of hydrogen atoms from various positions of the cellulose[14] to form peroxyl radicals in the presence O_2 according to Scheme 1. On the basis of extensive evidence from studies of irradiation of carbohydrates,[15] the reaction sequence shown below can be proposed to operate for cellulose in the presence of O_3/O_2. The associated rate constants are given in Table 1.

Initiation (this work)

$$\mathrm{O3} + \text{Lignin} \rightarrow \text{products} + \text{some } \mathrm{OH}\bullet$$

Propagation

Note: R(OH)CH refers to structures 1, 2, 3 and 6 while RCH denotes structures 4 and 5.

$$\mathrm{OH}\bullet + \mathrm{R(OH)CH} \rightarrow \mathrm{R(OH)C}\bullet \tag{1a}$$

$$\mathrm{OH}\bullet + \mathrm{RCH} \rightarrow \mathrm{RC}\bullet \tag{1b}$$

$$\mathrm{R(OH)C}\bullet + \mathrm{O_2} \rightarrow \mathrm{R(OH)COO}\bullet \tag{2a}$$

$$\mathrm{RC}\bullet + \mathrm{O_2} \rightarrow \mathrm{RCOO}\bullet \tag{2b}$$

$$\mathrm{R(OH)COO}\bullet \rightarrow \mathrm{RCO} + \mathrm{HO_2}\bullet \tag{3}$$

$$\mathrm{RCOO}\bullet + \mathrm{OH^-} \rightarrow \mathrm{RCOH} + \mathrm{O_2^-}\bullet \tag{4}$$

$$\mathrm{O_2^-}\bullet + \mathrm{O_3} + \mathrm{H_2O} \rightarrow \mathrm{OH}\bullet + 2\mathrm{O_2} + \mathrm{OH^-} \tag{5}$$

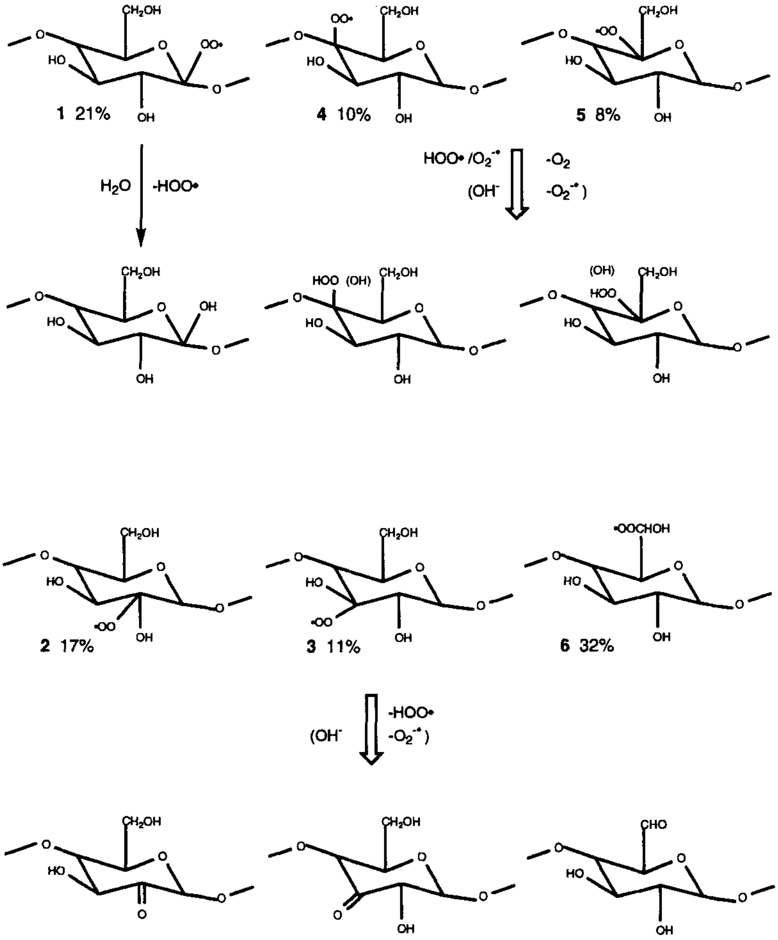
$$\mathrm{HO_2}\bullet \rightleftharpoons \mathrm{H^+} + \mathrm{O_2^-}\bullet \tag{6}$$

$$2\mathrm{RCOO}\bullet \rightarrow 2\mathrm{RCO}\bullet + \mathrm{O_2} \rightarrow 2\mathrm{O_2^-}\bullet + \text{product} \tag{7a}$$

Termination

$$2\mathrm{RCOO}\bullet \rightarrow \mathrm{RCOOCR} + \mathrm{O_2} \tag{7b}$$

$$\mathrm{ROO}\bullet + \mathrm{HO_2}\bullet \rightarrow \mathrm{ROOH} + \mathrm{O_2} \text{ (positions 4 and 5)} \tag{8a}$$


1 21%
4 10%
5 8%
H₂O
-HOO•
HOO• /O₂⁻•
(OH⁻
-O₂
-O₂⁻•)
2 17%
3 11%
6 32%
•OOCHOH
HOO (OH)
(OH)
HOO
-HOO•
-O₂⁻•)
CH₂OH
CHO
OO•
•OO
HO
OH
O

SCHEME 1.

TABLE 1

Rate Constants for Reactions

Reaction	Rate Constant	Reference
1a, 1b	$\approx 10^9$ $M^{-1}s^{-1}$	13
2a, 2b	$\approx 10^9$ $M^{-1}s^{-1}$	13
3	>400 s^{-1}	14
4	<1 s^{-1}	14
5	1.5×10^9 $M^{-1}s^{-1}$	13
6	pK_a 4.8	15
7a, 7b	10^4-10^6 $M^{-1}s^{-1}$	13
8a, 8b	$\approx 10^7$ $M^{-1}s^{-1}$	16
9a	9.8×10^5 $M^{-1}s^{-1}$	13
9b	9.7×10^7 $M^{-1}s^{-1}$	13

$$ROO\bullet + O_2^{-}\bullet \rightarrow ROO^- + O_2 \qquad (8b)$$

$$2HO_2\bullet \rightarrow O_2 + H_2O_2 \qquad (9a)$$

$$HO_2\bullet + O_2^{-}\bullet \rightarrow O_2 + HO_2^- \qquad (9b)$$

The pH-dependent rate constant of superoxide dismutation is given by

$$k = ([H^+]^2 \text{ x } k_{9a} + [H^+] \text{ x } K_6 \text{ x } k_{9b})/([H^+]+K_6)^2 \qquad [3]$$

where $pK_6 = 4.8$. As $HO_2\bullet$ is unreactive toward ozone, the pH dependence of superoxide reactivity with O3 is represented by

$$k = k_5 \text{ x } K_6/([H^+]+K_6) \qquad [4]$$

All positions but 4 and 5 (82% of all radicals) are chain-propagating peroxyl radicals. Expulsion of $HO_2\bullet$ from position 4 and 5 in Reaction 4 is slow but may be prone to OH^- catalysis.[14] Thus, in slightly acidic solution the peroxyl radicals 4 and 5 (totalling

~18 %) will eventually terminate the chain (reactions 7b and 8).[13] From the branching ratio of Reactions la and lb, a minimum chain length of 4.5 can be calculated.

Depolymerization Efficiency of OH• Radicals

The peroxyl radicals 1 and 4 will eventually lead to depolymerization of cellulose. The reaction of OH• radicals with cellobiose[17] in the presence of oxygen yields 13-18 % scission of the glycosidic linkage. Given the extra glycosidic linkages in cellulose, there should occur about 0.2-0.27 scissions per OH• radical. This figure is supported by data on depolymerization of alginic acid by OH• radicals which was found to have an efficiency of 0.22 scissions per OH• radical.[18]

Scope of the Investigation

To date, a large number of additives has been tested in several laboratories.[19] In spite of this, no consensus appears to have been reached about the chemical mechanisms underlying the viscosity loss during ozonation of pulp. This investigation had three principal objectives:

1. To settle the question about hydroxyl radical formation and its relevance during ozone bleaching.
2. To determine the selectivity of ozone towards lignin versus cellulose.
3. To elucidate the role and amount of peroxides formed during ozonation of pulp.

EXPERIMENTAL

Modified cooked and oxygen-delignified softwood kraft pulp (kappa number = 8.9) was treated with different radical scavengers and ozone. The metal content of the pulp was as follows: Mn, 31 ppm; Fe, 27 ppm; and Cu, 0.2 ppm. The ozone bleaching was performed at high consistency (*ca.* 39 %) in a rotating sphere glass reactor. Ozone was generated from oxygen in a Fischer ozone generator. The ozone concentration was measured by iodometric titration after absorption in a potassium iodide solution. The same method was used for residual ozone.

Before ozone bleaching, the pulp was treated with acid (2% consistency in dilute sulfuric acid at pH 2) and washed with deionised water. Then the pulp (at 2% consistency) was impregnated with a solution containing the radical scavenger. For basic solutions, HCO_3^-/CO_3^{-2} or borate buffers with the desired pH were used. The pH given in table 2 is the reading of the pH meter. Clearly, when substantial amounts of scavengers are added these readings become distorted and should not be taken at face value.

After 10 min the pulp was filtered and concentrated to about 35% consistency. This was followed by fluffing to a final consistency of about 40%. The pulp was flushed with oxygen before and after ozone treatment. After ozonolysis the consistency of the pulp was reduced to *ca.* 10% by addition of deionised water and the pH was measured. The pulp was then washed with deionised water. Alkaline extraction was performed by mixing 4-6 mL of a 0.5 M NaOH solution with the pulp (at 10% consistency) until a pH of 11.6-12.2 was obtained. The alkaline pulp was placed in a plastic bag which was heated for 1 h in a water bath at 60°C. The bag was then cooled, the pH was measured, and the pulp was washed again with deionised water.

Measurements of kappa number, ISO-brightness, and viscosity were performed according to SCAN standards. Before viscosity determinations the pulp was reduced with sodium borohydride.

Determination of peroxide content was achieved by means of iodometry with ammonium molybdate catalyst. The pulp was soaked for 30 min in water (1%

consistency), filtered, and washed. The collected filtrate was titrated to obtain the amount of extractable peroxide. Subsequently, the pulp was suspended in water and the slurry was analyzed for bound peroxide. In a control experiment the stability of the peroxides in the pulp was tested by allowing the pulp to stand for 1 h after irradiation prior to analysis of peroxides. No decrease of the peroxide content was found. Copper numbers were determined as described by Hägglund.[20]

RESULTS AND DISCUSSION

Ozonation at pH 2

Table 2 summarizes the experiments that were been done at pH 2 with various additives. Only additives whose reactivities toward both OH• and O_3 were known[13] were used. While moderately reactive towards OH• radicals, alcohols are almost inert towards O_3. Alcohols are known to undergo Reaction 3, the life times, $(k_3)^{-1}$, of $CH_2(OH)OO\bullet$ and $CH_3CH(OH)OO\bullet$ being >100 and 20 ms, respectively.[13] For CH_3CH_2OH to fully suppress viscosity losses the lifetime of $CH_3CH(OH)OO\bullet$ with respect to radical-radical annihilation should be <<20 ms in the present system. DMSO is an efficient OH• radical scavenger, but O_3 attacks it at a rate similar to its reaction with pulp. Figure 1 illustrates the effect of added DMSO or ethanol on ozonized pulp. It is apparent that the loss of viscosity is less as the concentration of the scavenger is increased, and that at similar concentrations the viscosity is higher for DMSO compared with ethanol. These observations, combined with the fact that DMSO is a more efficient OH• scavenger than ethanol, identify OH• as a major cellulose degradation agent during ozonolysis of pulp. However, below *ca.* kappa 2 the change of the curvature attests to another cellulose degrading reaction. From Equation 2 it is estimated that 17 % of the ozone reacts with cellulose at kappa 1. Thus, we conclude that below kappa 2, cellulose is degraded in a direct reaction with ozone.

TABLE 2

The Effect of Additives on Ozonation at pH 2

Additive	Viscosity (mL/g)	Final Kappa	Ozone[d] (mg/g)	pH	Brightness %
b	778	8.9	-	-	42.0
c	791	8.9	-	-	44.3
-	592	1.0	7.55	2.09	78.0
1 M *t*-BuOH	577	<1.0	7.31	1.96	77.1
t-BuOH (100%)[a]	719	1.0	6.74	≈2.59	76.2
1 M MeOH	665	1.0	7.03	2.04	78.0
MeOH (100%)[a]	715	1.0	6.90	≈2.52	76.8
1 M EtOH	677	<0.9	7.29	2.01	77.9
1 M EtOH	716	1.6	5.27	2.01	72.4
1 M EtOH	736	2.4	3.93	2.10	66.0
3 M EtOH	709	1.0	7.22	2.08	75.9
3 M EtOH	743	1.5	5.48	2.08	72.1
3 M EtOH	760	2.4	3.94	2.04	65.1
EtOH (100%)[a]	755	2.5	10.7	2.60	69.7
1 M HCOOH	648	1.0	8.52	1.84	75.3
1 M DMSO	747	1.2	10.5	2.06	72.4
1 M DMSO	742	1.5	8.06	2.05	72.2
1 M DMSO	771	2.1	5.37	2.01	65.7
1 M DMSO	775	3.6	3.32	2.02	60.0
3 M DMSO	775	2.1	8.42	2.15	66.3
3 M DMSO	776	2.6	6.10	2.15	64.4
3 M DMSO	785	3.6	3.97	2.15	59.5
6 M DMSO	787	3.2	10.5	2.40	61.4
6 M DMSO	784	3.4	7.40	2.40	61.4
6 M DMSO	786	4.5	3.95	2.46	56.1
DMSO (100%)[a]	797	6.0	41.1	≈2.92	50.8

[a] (10^{-3} M H_2SO_4) added, [b] untreated pulp, [c] same as b but extracted with alkali, and [d] ozone consumed

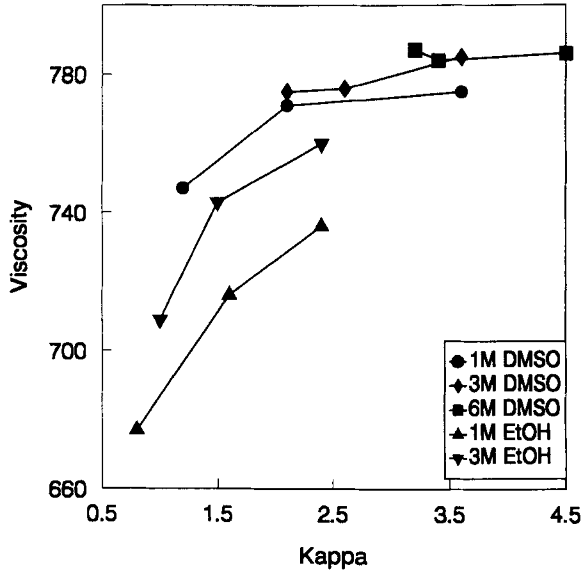
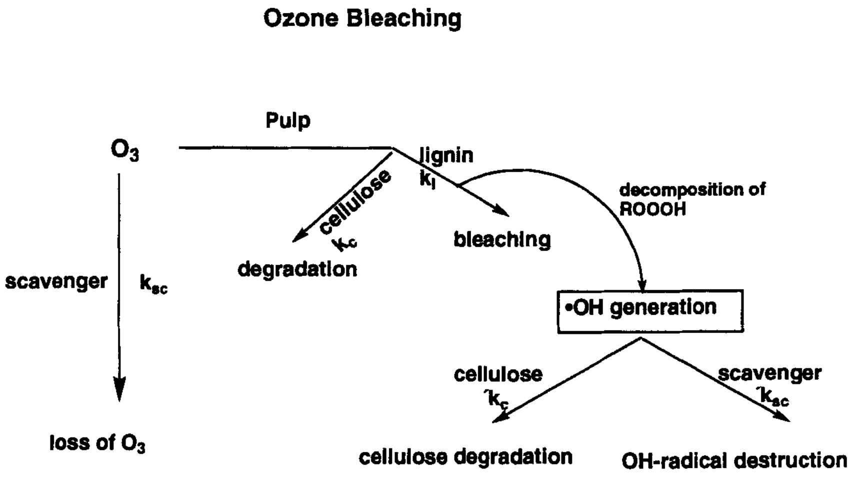


Figure 1. Viscosity-Kappa relationship in ozonolysis of pulp at pH 2 in the presence of OH• radical scavengers. ■ 6 M DMSO, ◆3 M DMSO, ● 1 M DMSO, ▲ 1 M EtOH, ▼ 3 M EtOH

In addressing the issue of the part played by OH• more quantitatively, extensive use will be made of competition kinetic techniques. An outline of ozone bleaching in the presence of OH• scavengers is given in Scheme 2. The curved arrow indicates the formation of OH•. If the scavenger is chosen properly, i.e., the scavenger should not produce OH• when reacting with O_3, the yield of OH• will become proportional to the amount of O_3 reacting with the pulp. Therefore, to make sure that the amount of OH• produced did not vary from one experiment to another, ozonation was run to the same final kappa, i.e. Δkappa was kept constant. Under these condition the amount of cellulose destroyed is proportional to the fraction of the OH• that react with the cellulose. The latter is given by Equation 5.



Scheme 2

$$'k_c[C]/('k_c[C]+ 'k_l[L]+ 'k_{sc}[Sc]) \qquad [5]$$

Here, as in Scheme 2, C, L and Sc are abbreviations for cellulose, lignin and scavenger, respectively. Furthermore, $'k_l[L] << 'k_c[C]+'k_l[L]+'k_{sc}[Sc]$ (vide infra). We also assume proportionality between the degree of cellulose destruction and the loss of viscosity, ΔV. Strictly speaking, viscosity change is not linearly related to the number of chain breaks in the cellulose. However, as the ΔV interval covered in our analysis is no more than 100 mL/g, direct proportionality between these two quantities should be a satisfactory approximation. Combination of the above points yields Equation 6.

$$\Delta V/\Delta \text{kappa} = (\Delta V_o/\Delta \text{kappa})'k_c[C]/('k_c[C] + k_{sc}[Sc]) \qquad [6]$$

ΔV_0 is a proportionality constant, equal to the viscosity change in the absence of any scavenger.

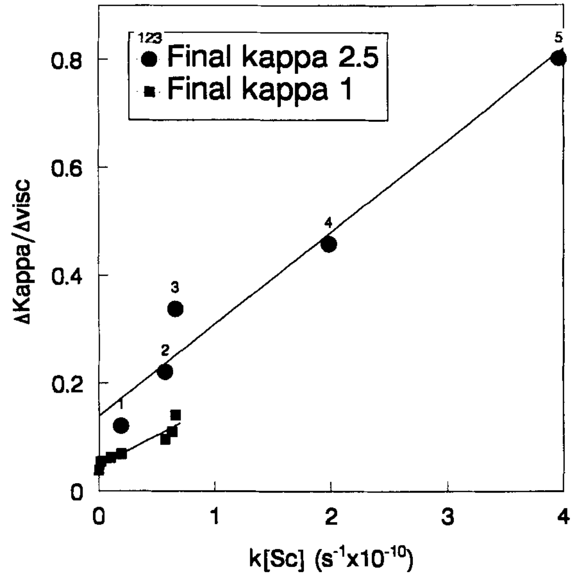


Figure 2. ΔKappa/Δviscosity measured upon ozonolysis of pulp at pH 2 as a function of the rate of OH• radical scavenging. ● Final kappa 2.5, Point 1, 1 M EtOH; Point 2, 3 M EtOH; Point 3, 1 M DMSO; Point 4, 3 M DMSO; and Point 5, 6 M DMSO. ■ Final kappa, the values are taken from Table 1.

By inversion the expression can be linearized:

$$\Delta\text{kappa}/\Delta V = (\Delta\text{kappa}/\Delta V_o)(1 + {}'k_{sc}[Sc]/{}'k_c[C]) \qquad [7]$$

Obviously, if OH• is an intermediate in the degradation of cellulose, a plot of Δkappa/AV *vs* $'k_{sc}[Sc]$ will yield a straight line, such as shown in Figure 2. The linear relationship in Figure 2 constitutes strong support for hydroxyl radicals being formed according to Scheme 1. The values for kappa 1 were taken from Table 2, while those pertaining to kappa 2.5 were interpolated/extrapolated from Figure 1. In the second set, ethanol and dimethyl sulfoxide were employed as OH• scavengers. The rate constants for their reaction with OH•, $'k_{sc}$ of 1.9×10^9 and 6.6×10^9 $M^{-1}s^{-1}$, respectively, were taken from the literature.[13] The intercepts in Figure 2 correspond to a viscosity loss, due to OH•, of *ca.* 10% in going from kappa 8.9 to 2.5. Had only OH• been responsible for cellulose degradation, the intercepts at the final kappa numbers 1 and 2.5 would have been equal. As can be seen, however, the viscosity loss at the final kappa of 1 is as high as 22% of which only *ca.* 10% is caused by OH•. We propose that the remaining loss of 12% is due to the direct reaction of O_3 with the cellulose. This is supported by the closeness of the figure, 17%, which is estimated from Equation 2 at kappa = 1. *The direct reaction between ozone and cellulose puts a lower limit to the kappa number (ca. 2) to which ozonation can be driven, even in the presence of efficient OH• scavengers.*

Ozonolysis at pH 10

In ozonolysis of pulp it is common knowledge that the reaction should be performed at pH 2-3 to minimize cellulose degradation. If the pH effect is due to an increased flux of OH• radicals with increasing pH, the addition of radical scavengers at pH 10 should show a dramatic effect. At pH 10, carbonate anion appeared to be a promising candidate for a scavenger since the rate constant for its reaction with ozone has been reported to be <0.01 $M^{-1}s^{-1}$.[21] In addition, CO_3^{-2} reacts with OH• to yield the carbonate radical, CO_3^{-}•. We have determined that the lignin/cellulose selectivity of CO_3^{-}• to be $>10^3$ (cf. OH• selectivity of ~7). The high pH results are compiled in Table 3. Some of these data are also presented in graphical form in Figures 3a and 3b. In both figures the lines pertain to carbonate. Point 1 refers to pulp without any additive while point 2 denotes pulp with 1 M DMSO added. Contrary to our expectations the data show that during ozonolysis carbonate does not protect cellulose against degradation. In addition, it also leads to a 2-fold increase in the consumption of O_3 (cf. points 1 and 3 in figs. 3a and 3b). This indicates a reaction between O_3 and carbonate which will eventually generate OH•. It also points to a much higher reactivity between ozone and carbonate than reported.

TABLE 3

The Effect of Additives on Ozonation at pH 9-10

Additive	Viscosity (mL/g)	Final Kappa	Ozone[a] (mg/g)	pH	Brightness %
0.01 M CO_3^{-2}	466	1.4	9.79	9.80	74.86
0.5 M CO_3^{-2}	461	3.8	12.83	9.65	59.12
0.5 M CO_3^{-2}	361	2.8	26.18	9.68	64.85
0.5 M CO_3^{-2}	277	2.3	35.30	9.99	70.06
0.05 M CO_3^{-2}	431	2.9	11.40	9.99	63.06
0.1 M Borate	349	2.5	13.90	9.40	70.15
1 M *t*-BuOH[b]	359	2.2	13.34	9.45	72.99
1 M DMSO[b]	726	2.2	8.81	9.34	66.64

[a]Ozone consumed, [b]0.1 M borate added

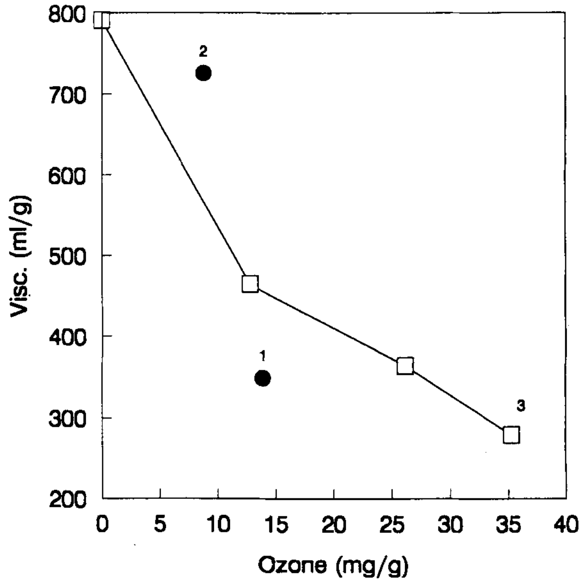


Figure 3a. □Variation of pulp viscosity as a function of O_3 charge at pH 10 (0.5 M CO_3^{-2} + 0.5 M HCO_3^-). ● Pulp ozonized to the kappa number of Point 3 in the absence of carbonate: Point 1, borate buffer; Point 2, borate buffer and 1 M DMSO.

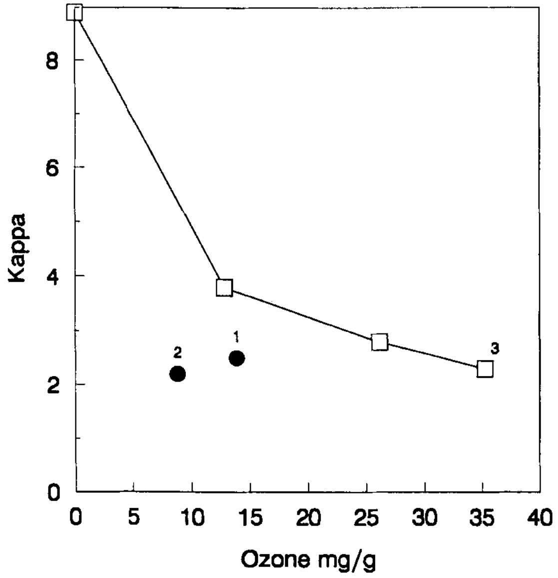


Figure 3b. □Variation of pulp kappa number as a function of O_3 charge at pH 10 (0.5 M CO_3^{-2} + 0.5 M HCO_3^-). ● Pulp ozonized to the kappa number of Point 3 in the absence of carbonate: Point 1, borate buffer; Point 2, borate buffer and 1 M DMSO.

Furthermore, addition of DMSO prevents loss of viscosity and allows for a more efficient use of O_3, (cf. points 1 and 2). The latter finding unambiguously proves an increase in the flux of OH• radicals at high pH.

The Rate Constant for Ozone Reacting With Carbonate

We measured the rate constant between ozone and $C0_3^{-2}/HCO_3^-$by means of an ozone electrode. To one liter of water containing 3 x 10^{-5} M O_3, excess $C0_3^{-2}$ (2 x 10^{-4} - 1 x 10^{-3} M) or HCO_3^- (1 x 10^{-3} - 5 x 10^{-3} M) was added and the decay of ozone was measured as a function of time. The decay was exponential and yielded the following second order rate constants: $k(O_3 + CO_3^{-2}) = 120\ M^{-1}s^{-1}$ and $k(O_3 + HCO_3^-) < 10^{-1}\ M^{-1}s^{-1}$. As these values exceed by far the corresponding literature

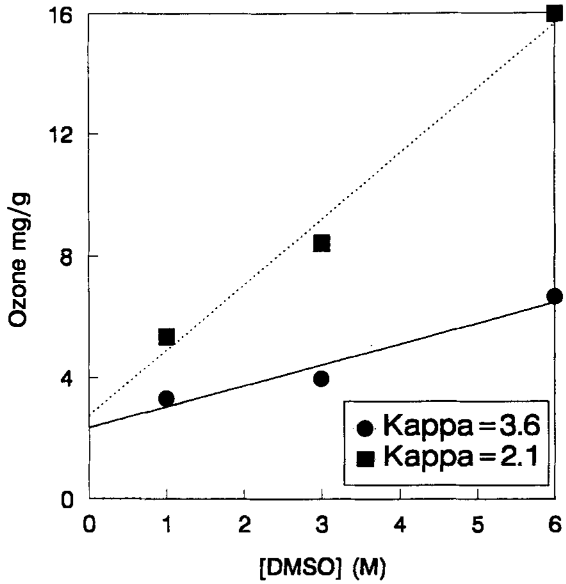


Figure 4. Ozone consumption as a function of the amount of DMSO added. ● Ozonolysis to pulp kappa 3.6. ■ Ozonolysis to pulp kappa 2.1.

data,[21] one should beware of taking values reported for ozone reactivities in carbonate-buffered systems at face value.

Reaction of Ozone with HC Pulp

Figure 4 shows the amount of O_3 which has to be added to reach a constant kappa number as a function of the DMSO concentration. The necessity for increasing the ozone addition with increasing DMSO concentration is a consequence of the reaction between O_3 and DMSO. Given that all experiments start with the same kappa value and taking account of the competition in Scheme 2, it follows that as long as the Δkappa is kept constant:

$$\Delta\text{kappa} = A[O_3]r_p/(r_p + k_{sc}[\text{DMSO}]) \qquad [8]$$

where $r_p = r_l + r_c = k_l[\text{lignin}]_{mean} + k_c[\text{cellulose}]$ are the rate constants (s^{-1}) for the reactions of lignin and cellulose with ozone under HC conditions. The term $[\text{lignin}]_{mean}$ is the integral mean value of the lignin present during ozonolysis. The term $[O_3]$ is the amount of ozone consumed. The term A is the ratio between kappa number and lignin content. The equation can be rewritten as:

$$[O_3] = \Delta \text{kappa}(1 + k_{sc}[\text{DMSO}]/r_p)/A \qquad [9]$$

In Figure 4 the lines are linear least squares fits according to Equation 9. The intercept divided by the slope yields r_p/k_{sc}. According to this model r_p/k_{sc} will be proportional to $[\text{lignin}]_{mean}$, which clearly varies with the final kappa number. This model is simplified in that the diffusion of ozone through the fiber is neglected. The farther that ozone has to diffuse through the DMSO dissolved in the intra-crystalline water of the fiber before it strikes lignin, the larger will be the chance of it will react with DMSO. As a consequence, the ratio r_p/k_{sc} will decrease more with decreasing final kappa number than would be predicted by Equation 9. Since k_{sc} is constant either way, the result is a formal reduction of r_p. Indeed, as the figure discloses, the intercept/slope decreases with decreasing final kappa number. Employing the reported $k_{sc} = 8\ M^{-1}s^{-1}$ for DMSO[13] we calculated r_p to be 26 and 10 s^{-1} for final kappa numbers of 3.6 and 2.1, respectively.

At pH 10 the increase in ozone consumption between points 1 and 3 (Fig. 3b) amounts to 250 %. This implies that the rate of O_3 reacting with $C0_3^{-2}$ is 2.5 times greater than that of ozone reacting with HC pulp. By combining the rate constant ~120 $M^{-1}s^{-1}$ with the concentration of $C0_3^{-2}$ (0.5 M) we estimated the effective rate of O_3 reacting with the HC pulp, r_p, to be ~60 s^{-1}. The higher r_p at pH 10 is indicative of an increase in OH• flux, caused mainly, if not exclusively, by an increase in the chain length (reactions 1-7a). Clearly, this increase can in no way be ascribed to the direct reaction of OH^- with O_3, as the rate constant is only 7 x 10^{-3} s^{-1}-1 at pH 10, i.e., no more than 0.01% of the overall consumption rate of O_3.

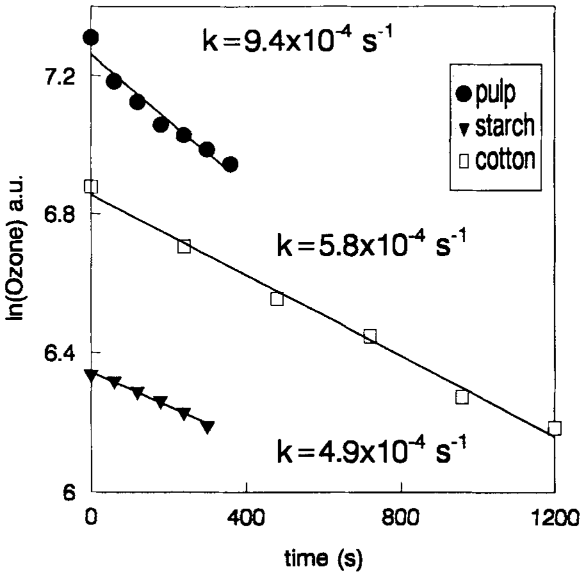


Figure 5. First-order kinetic plots of ozone destruction by carbohydrates having a concentration of 1 g/dm^3. □ $NaBH_4$ reduced cotton linters at pH 2 and 7 in the presence of 8 g/dm^3 t-BuOH. ▼ Starch and ● Cl_2 bleached pulp, both in neutral solution.

The Rate Constant for Reaction of Ozone with Cellulose.

In Figure 5 first-order plots of O_3 decay in the presence of fully bleached pulp, sodium borohydride-reduced cotton linters, and starch are presented. The ozone decay was monitored with an ozone electrode. Gratifyingly, the three rates agree within a factor of 2. They pertain, however, to LC conditions. If we multiply these rates by 180, the approximate molecular weight of the β-glucosidic subunit, we obtain a value of *ca.* 0.1 $M^{-1}s^{-1}$. This value is lower by a factor of *ca.* 4 than 0.45 $M^{-1}s^{-1}$ and 0.48 $M^{-1}s^{-1}$, the reported values for glucose and methyl β-D-glucopyranoside, respectively.[22] This could be taken to imply that, on the average, only every fifth subunit in the fiber is accessible to O_3. Scaled to HC conditions, i.e., from 1 g pulp/dm^3 water to 667 g pulp/dm^3 water, we obtain $r_c \approx 0.5$ s^{-1}.

TABLE 4

Copper Number Obtained Upon Ozonolysis of Fully Bleached Pulp

Additive	Ozone Consumption (mg/g)	ΔCu Number (mL/g)
------	1.98	0.64
DMSO 1 M	11.32	0.33
DMSO 1 M	19.90	0.51

In Table 4 we have compiled data on cellulose damage (Cu number) and ozone consumption in the presence and absence of DMSO during ozonolysis of cellulose. By plotting the ratio of ozone consumption to the increase in Cu number against the DMSO concentration we obtained an intercept/slope = $r_c/k_{sc} = 0.09\ M^{-1}$. Multiplying this value by $k_{sc} = 8\ M^{-1}s^{-1}$ we obtained an $r_c \approx 0.7\ s^{-1}$, in excellent agreement with the above value.

Selectivity of Ozone Toward Lignin and Cellulose

As was discussed above, the selectivity of ozone towards lignin versus cellulose is $\approx k_l/k_c$. As $r_p = r_l + r_c$ and $r_l >> r_c$, $r_l \approx r_p$, the reactivity ratio, r_p/r_c will drop from 52 at kappa 3.6 to 20 at kappa 2.1. Using conversion factor of 0.152 % lignin per kappa unit, and utilizing 6.2 as the mean kappa number during bleaching from kappa 8.9 to kappa 3.6, the selectivity can be calculated to be 5700. Similarly, using 5.5 as the mean kappa when kappa drops from 8.9 to 2.1, the selectivity, $k_l/k_c = 2400$. We thus note that, despite the above mentioned neglect of ozone diffusion, a reasonable internal consistency prevails between this experimental result and the selectivity ratio, $k_l/k_c = 3000$, estimated from model compounds.

Formation of Peroxides

Figure 6 summarizes our results pertaining to the determination of peroxides generated during HC ozonation of pulp at pH 2. The results demonstrate that both

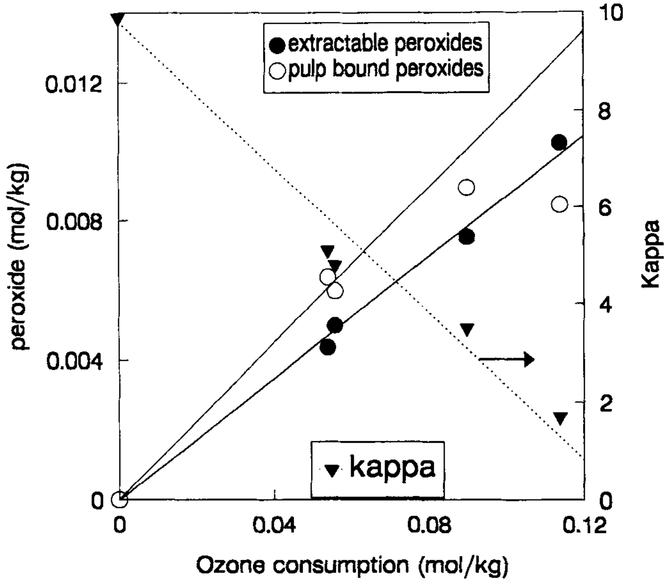
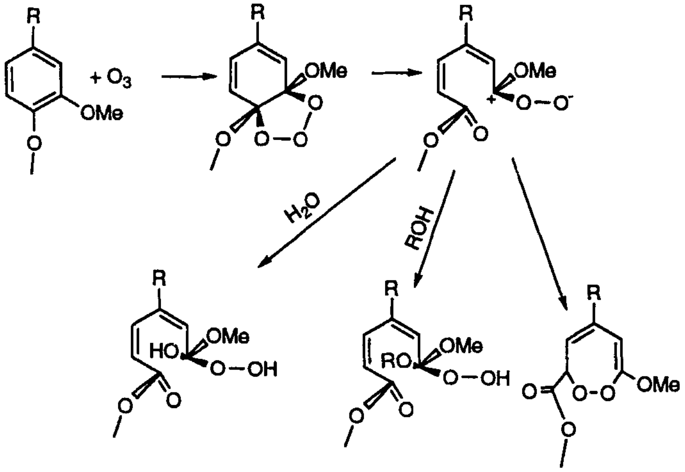


Figure 6. Peroxide yield and kappa number as a function of ozone consumption during HC ozonolysis of pulp at pH 2. ● Extractable peroxides, ○ pulp-bound peroxides, and ▼ kappa number.

kappa number reduction and peroxide formation are essentially proportional to ozone consumption. It then follows that, under the present conditions of ozonation (HC, pH 2, 25o C) O_3 does not degrade the hydroperoxides formed. This is in keeping with the reported low reactivity of O_3 towards H_2O_2 $\{k(O_3 + H_2O_2) = 0.04\ M^{-1}s^{-1}\}$.[23] The higher reactivity of HO_2^- $\{k(O_3 + HO_2^-) = 5.5 \times 10^6\ M^{-1}s^{-1}\}$[24] will set an upper limit to the pH (ca. 8) at which radical formation *via* hydroperoxide-ozone reactions can be neglected.

How then are peroxides formed in 0_3-lignin reactions? It is well established that ozone attack on aryl compounds results in a reaction sequence similar to that found for olefins.[25,26] The special feature in water is the interception by H_2O of the



Scheme 3

Crigee intermediate to form α-hydroxy hydroperoxides (Scheme 3). From theoretical considerations,[27] as well as recent experiments, it transpires that at pH 228 and 729 the lifetimes of α-hydroxy hydroperoxides with respect to H_2O_2 expulsion at pH 2 and pH 7 are known to be *ca.* 100 s.[28,29] Thus in our experiments, the H_2O_2 was probably derived from α-hydroxy hydroperoxides. As the bound peroxides cannot be α-hydroxy hydroperoxides, we have to consider other possibilities. Reasonable alternatives, presented in Scheme 3, comprise interception of the Crigee intermediate by a non-aqueous hydroxyl group to form α-acetal hydroperoxides or cyclic peroxides. We note that such intermediates would contain conjugated dienic entities, which are known to be reactive towards ozone. These dienes bear electron-rich functional groups. It is therefore conceivable that some, or even most of their degradation products with ozone may not contain peroxidic functions. Such a possibility would at least rationalize the finding that the peroxide yield per O_3 consumed is only 20%. The low yield of peroxides could be rationalized by assuming that, once formed, they might be decomposed by transition metal ions in the pulp and subsequently initiate the chain reaction. This possibility was suggested by the authors of Reference 7, where ozonation was performed under LC conditions. However, a later study[30] under similar conditions by the same authors reveals two interesting things. First, the hydrogen peroxide yield found was *ca.* 7%, which compares with the yield of extractable peroxides in the present work (*ca.* 8%, see Fig. 6). Secondly, addition of 100 ppm Fe^{+2}, the most cellulose-damaging metal,[7] lowered the hydrogen peroxide yield from 7% to merely 6%. These findings confirm that the low peroxide yields are not due to the effect of transition metal ions.

Initial Production of Radicals

Three alternative hypotheses for the production of radicals can be formulated:

1. Radicals are generated in the reaction between lignin and ozone. As there is a branching between delignification and radical production this hypothesis leads to $S = \Delta\text{kappa}/\Delta\text{viscosity} = \text{constant}$.

2. Radicals are generated from ozone in its reaction with non lignin compounds, e.g. cellulose, water-mediated self-decomposition, or a catalytic metal ion reaction.[31]

3. Radicals are generated in a catalytic reaction between transition metals and the hydrogen peroxide formed during ozonolysis.[7]

According to the second hypothesis, OH• are produced in reactions which compete with the ozone-lignin reaction. These are pseudo-first-order reactions where virtually no reactant except ozone is consumed, i.e., we can assign an effective constant rate r to them. For the selectivity, the relationship $S \propto k_l[\text{lignin}]/r \propto \text{kappa}$ should then hold. However, from data of Lindholm[3] it is evident that, as the kappa number is decreased from 25 to 5, the selectivity remains almost constant. Thus, hypothesis 2 would seem to be ruled out by experiment. For hypothesis 3 to operate there has to exist a mechanism whereby the metal is reduced. The radicals produced in the reaction sequence la-2-3 are reducing. In every turnover some OH• will undergo reaction lb, terminating the chain and leaving the metal in its oxidized form. Thus, the chain will not be self-sustained. However, in a flow of ozone-generated reducing radicals, transition metals might, through their reaction with hydrogen peroxide, produce some extra OH•. Taken together, experimental evidence and mechanistic considerations would seem to favor hypothesis 1.

Mechanism of Radical Formation in the Ozone-Lignin Reaction

Besides being a good electrophile, ozone is also expected to be a reasonably strong one-electron oxidant, judging by its redox potential[32] of 1.01 V *vs* NHE. Applying the Marcus theory[33] of electron transfer to the reaction of ozone with 4-alkyl veratroles,[34] the rate constant for electron transfer (reaction 10) is predicted to be on the order of 10 $M^{-1}s^{-1}$.

$$O_3 + \text{4-alkyl veratrole} \rightarrow O_3^{\bullet -} + \text{4-alkyl veratrole}^{+} \qquad (10)$$

In combination with the total rate of ozone attack on 4-alkyl veratrole the fraction of radical formation comes out around 1%.

The insertion of O_3 into sp^3 C-H bonds is a reaction that forms unstable hydrotrioxides, ROOOH, which are believed, to some extent, to decompose into radicals.[35,36] As insertion of O_3 into R-H is concomitant with the rupture of the C-H bond, the efficiency of this reaction is clearly related to the bond strength. Benzylic C-H bonds with a strength of *ca.* 350 kJ/mole are significantly weaker than the C-H bonds in cellulose (*ca.* 390 kJ/mole) and should be the main target of this mode of ozone attack. Similarly, any residual phenol should yield some OH• with O_3. In ozonation studies of model compounds at pH 2 the yield of OH• per ozone reacted was found to be 3.4% with veratryl alcohol and <10% for a number of undissociated phenols.[37] The above findings taken together support the picture of OH• formation to the extent of a few percent in the direct reaction of O_3 with lignin. *In conclusion, radicals are primarily generated in the reaction of ozone with lignin.*

The Flow of OH• in the Fibers

The intercept in Figure 2 yields a viscosity loss of 10% subsequent to the consumption of 0.082 moles ozone by 1 kg pulp (final kappa = 2.5). According to Reference 38, a viscosity loss of 15% corresponds to 6×10^{-4} moles of chain breaks per kg pulp. Taking the depolymerization efficiency of OH• to be 0.25, we calculated that *ca.* 2 OH• are generated per 100 ozone molecules consumed. We believe this figure to be correct within a factor of 2-3, i.e., 0.5-5% of ozone reacts with lignin to generate OH•. The rate of production of the radicals is thus *ca.* 2% of the delivery rate of O_3. The latter is 1 mg/g pulp/min. With a rate constant[13] of 4×10^8 $M^{-1}s^{-1}$ for radical annihilation, this yields a radical lifetime of *ca.* 10 ms. This value is in agreement with our earlier conclusion, i.e., in order for ethanol to protect viscosity the lifetime of its peroxyl radical, $CH_3CH(OH)OO$• must be shorter than 20 ms.[39]

Chain Length, Effect of pH, and Rate of Ozone Delivery

The amount of $O_2^{\bullet -}$ varies strongly with the pH according to Reaction Equilibrium 6. Given that the rates of Reactions 1-3 exceed 103 s^{-1} under practical conditions, the rate-determining step, below pH ≈ 3, in the radical chain propagation will be Reaction 5. At pH 2 the rate of Reaction 5 becomes so slow as to compete with termination. Then, Reactions 8 and 9 will be the main termination reactions and the chain length will be shorter than 4.5, the value estimated above. At pH values around and above $pK_a(HO_2\bullet) = 4.8$, Reaction 5 is so fast that the chain will continue until virtually all radicals have been converted into RCOO• (Reaction lb). Termination then proceeds via Reaction 7b, and the chain length will depend on the branching ratios la/lb and 7a/7b of Reactions 1 and 7.

Varying the rate of ozone delivery should have a marginal effect unless it is so low ($<\sim10^{-5}$ mole/kg/s) that Reaction 4 ($k_4 \approx 1\ M^{-1}s^{-1}$)[12] becomes important.

CONCLUSIONS

The present model could be refined by incorporating ozone diffusion through the fibers. To achieve this one would have to fine tune the kappa change *vs.* ozone charge experiments. While this would improve the numbers we feel that the present model contains most relevant aspects which are summarized below.

Radicals are generated in the reaction of ozone with lignin. We propose that superoxide radicals diffuse within the fibers. Inside the fibers the chain reaction sequence 1-9 will be set up, which will cause extensive damage to cellulose.

By removing OH• by addition of efficient OH• scavengers, pulp can be bleached with ozone to kappa numbers around 2 without loss of viscosity.

The direct reaction between ozone and cellulose puts a lower limit to the kappa number (*ca.* 2), to which ozonation can be driven.

Several research strategies to minimize viscosity losses in ozone bleaching can then be envisaged:

1. It might be possible to reduce the rate of OH• formation by lowering the temperature. This is because the suggested modes of radical formation are expected to have higher activation energies than ozone addition to aromatics.
2. In order to scavenge OH• to an acceptable degree, concentrations of additives around 1 M are needed. Are there any cheap additives, e.g. nitrated lignosulfonates or nitrated polystyrene sulfonates, which could be utilized and perhaps recycled?

3. To explore an efficient superoxide decomposer in order to rapidly terminate the $O_2\bullet^-$ mediated chain reaction (Reactions 1-7a). Successful resolution of this issue could have the additional benefit of allowing ozonation to be performed at neutral pH.

ACKNOWLEDGMENT

The financial support of the Swedish Pulp and Paper Research Institute (STFI) is gratefully acknowledged. We also wish to express our gratitude to various members of the staff of STFI for helpful comments and suggestions.

REFERENCES

1. (a) Y. Zhang, On the Selectivity of Ozone Delignification During Pulp Bleaching, TRITA-PMT REPORT 1994:4, Royal Institute of Technology, Stockholm, (1994).
   (b) J. Gierer and Y. Zhang, Seventh International Symposium on Wood and Pulping Chemistry Proceedings, Vol. 2, p. 951-960, Beijing, China, (1993).

2. T. Eriksson and J. Gierer, J. Wood Chem. Technol., 5, 53 (1985).

3. C-A. Lindholm, 1987 Tappi International Oxygen Delignification Conference Proceedings, p. 155, San Diego, CA, June 7-11, 1987.

4. P.J. Balousek, T.J. McDonough, R.D. McKelvey, and D.C. Johnson, Svensk. Papperstidn., 9, R49 (1981).

5. J.L. Colodette, U.P. Singh, A.K. Ghosh, and R.P. Sing, Pulp & Paper, 67, 139 (1993).

6. Y. Ni, G.J. Kang, and A.R.P. van Heiningen, J. Pulp Paper Sci., 22, J53 (1996).

7. C. Chirat and D. Lachenal, 1994 International. Pulp Bleaching Conference Proceedings, p. 109, Vancouver.

8. T. Eriksson and J. Gierer, ISWPC, Poster presentation, p. 29, Vancouver (1985).

9. H. Kaneko, S. Hosoya, K. Iiyama, and J. Nakano, J. Wood. Chem. Technol., 3, 399 (1983).

10. J. Hoigné and H. Bader, Water Res., 17, 185 (1983).

11. J. Hoigné and H. Bader, Water Res., 17, 173 (1983).

12. (a) D. Lachenal, J. C. Fernandes, and P. Froment, EWLP 94, p 81 (1994). (b) A. R. P. van Heiningen, personal communication.

13. A.B. Ross, W.G. Mallard, W.P. Hellman, G.V. Buxton, R.E. Huie, and P. Neta, NDRL-NIST Solution Kinetics Database Ver. 2, NIST Standard Reference Data, Gaithersburg, MD, 1994.

14. M.N Schuchmann and C. von Sonntag, J. Water Supply Res. Technol.-Aqua, 38, 311 (1989).

15. C. von Sonntag, The Chemical Basis of Radiation Biology, p. 375-393, Taylor & Francis, London, 1987.

16. C. von Sonntag and H.-P. Schuchmann, Angew. Chem. Int. Ed. Engl., 30, 1229 (1991).

17. M.N. Schuchmann and C. von Sonntag, Int. J. Radiat. Biol., 34, 397 (1978).

18. S. Akhlaq, H.-P. Schuchmann, and C. von Sonntag, Environ. Sci. Technol., 24, 379 (1990).

19. N. Liebergott, B. van Lierop, and A. Skothos, 1991 TAPPI Pulping Conference Proceedings, p. 1-23, Orlando, FL.

20. E. Hagglund, Cellul. Chem. Technol., 11, 1 (1930).

21. J. Hoigné, H. Bader, W.R. Haag, and J. Staehelin, Water Res., 19, 993 (1985).

22. G. Pan, C.-L. Chen, H.-m. Chang, and J.S. Gratzl, 1981 Ekman Days Proceedings, Vol. 2, p. 132, Stockholm.

23. K. Sehested, H. Corfitzen, J. Holcman, and E.J. Hart, J.Phys. Chem.,96, 1005 (1992).

24. J. Staehelin and J. Hoigne, Environ. Sci. Technol., 16, 676 (1982).

25. P.S. Bailey, Ozonation in Organic Chemistry, Vol. 2, p. 18-42, Academic Press, New York, 1982.

26. S.D. Razumovskii and G.E. Zaikov, Ozone and its Reactions with Organic Compounds, p. 211-234, Elsevier, Amsterdam, 1984.

27. Present authors, unpublished results.

28. J. Etzel, Identifizierung und Charakterisierung der peroxidischen Reaktionsprodukte bei der Ozonisierung organischer Wasserinhaltsstoffe, Thesis, p. 52, Kernforschungszentrum Karlsruhe, KfK 5176, 1993.

29. X. Zhou and Y.-N. Lee, J. Phys. Chem., 96, 265 (1992).

30. C. Chirat and D. Lachenal, 8th ISWPC Proceedings, p. 293, Helsinki, 1995.

31. Any non-catalytic metal ion reaction is only a "one-shot" process, which will produce an amount of radicals corresponding to the metal ion content at the onset of ozonation.

32. U. Klaning, K. Sehested and J. Holcman, J. Phys. Chem., 89, 760 (1985).

33. L. Eberson, in Electron Transfer Reactions in Organic Chemistry, Springer Verlag, New York, 1987.

34. The values used:
$E^o(0_3/0_3{\bullet}^-)$ 1.01 V, Reference 27.
E^o(4-alkyl veratrole$\bullet^+$/4-alkyl veratrole) 1.40 V, M. Jonsson, J. Lind, T. Reitberger, T.E. Eriksen and G. Merenyi, J. Phys. Chem., 97, 11287 (1993).

Self exchange rates:
$O_3/O_3{\bullet}^-$, 100 $M^{-1}s^{-1}$, L.E. Bennett and P. Warlop, Inorg. Chem., 29, 1975 (1994).
(4-alkyl veratrole$\bullet^+$ /4-alkyl veratrole) 3 x 10^7 $M^{-1}s^{-1}$, Reference 28.

35. F. Kovac and B. Plesnicar, J. Am. Chem. Soc., 101, 2677 (1979).

36. F. Kovac and B. Plesnicar, J. Chem. Soc., Chem. Commun., 122 (1978).

37. T. Eriksson, M. Ragnar, and T. Reitberger, personal communication.

38. J. Lind, G. Merenyi, and N. O. Nilvebrant, J. Wood Chem. Technol., submitted for publication.

39. With a lifetime close to 20 ms the efficiency of ethanol as scavenger will be reduced, as for each OH• scavenged *ca.* 30 % will be regenerated. This can formally be viewed as a reduction of the rate constant between OH• and EtOH by the same amount.