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Overview of Ozone Bleaching

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OVERVIEW OF OZONE BLEACHING

by

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INTRODUCTION

The pulp and paper industry is exploring ways to reduce its impact on the environment. Reducing the formation of chlorinated organic compounds and the volume of discharged effluent are key areas for improvement. Bleaching with oxygen-based chemicals can serve the pulp and paper industry well in meeting both of these objectives. Ozone is one promising oxygen-based alternative.

Interest in ozone bleaching by the U.S. pulp and paper industry first emerged in the 1970s when environmental legislation in this country began in earnest. Considerable research was conducted in laboratory facilities and pilot plants at that time. Interest waned as it became clear that several problems could not be readily overcome with the existing technology, including poor selectivity, poor uniformity, and the high expense of generating ozone. However, interest in oxygen-based bleaching resurged in the 1990s due to the discovery of chlorinated dioxins and furans in pulp and paper mill effluents, increasing environmental regulation, and increasing public pressure. As a result, several ozone plants have been recently built in the United States, Canada, and Europe. Fourteen worldwide installations in 1995 have capacities ranging from 100 to 1600 tpd, and include three virgin fiber facilities in the U.S.

The chemistry, applications, and environmental benefits of ozone bleaching are reviewed in this paper.

OZONE CHEMISTRY

Ozone is an electrophilic, nonlinear, extremely potent oxidant with an oxidation potential of -2.07 eV ($O_3 + H^+ + 2 e^- \rightarrow O_2 + H_2O$). By comparison, Cl_2 has an oxidation potential of -1.4 eV ($Cl_2 + 2 e^- \rightarrow 2 Cl^-$). The high degree of reactivity of ozone and the heterogeneity of pulp allow numerous types of chemical reactions to take place during bleaching. Ozone reacts rapidly at sites of high electron density, such as the side chain double bonds and aromatic rings found in lignin, and more slowly at less activated sites, such as the C-H bonds typical in carbohydrates. The generally fast rates of ozone reactions make mass transport to the desired sites of attack critical for efficient and selective bleaching.

Reactions With Carbohydrates

Carbon-hydrogen bonds in many saturated compounds are susceptible to cleavage by ozone, including the activated anomeric carbon-hydrogen bonds in carbohydrates. Highly reactive hydrotrioxide intermediates are produced from the ozonation of acetals,¹⁻³ including glucosidic acetals.⁴⁻⁶ Ozonation of ethers,⁷⁻⁹ aromatic aldehydes,^{7,10,11} and saturated hydrocarbons^{7,12} also produces hydrotrioxides. When there is an oxygen atom adjacent to the insertion site, the hydrotrioxide may be stabilized by an intramolecular hydrogen bond, forming a six-membered ring. Several mechanisms have been proposed for the formation of the hydrotrioxides, including a concerted 1,3 dipolar insertion (Fig. 1a), hydride transfer (Fig. 1b), hydrogen abstraction (Fig. 1c), and an initial attack at acetalic or etheric oxygens (Fig. 1d).

Most kinetic data, solvent effects, substituent effects, stoichiometry, and thermochemical calculations support either the concerted insertion,^{1,7,10,13} or the hydride transfer.^{7,12} However, attack by ozone on compounds with highly acidic α hydrogens of -CHOR groups, forming tetroxide intermediates, has also been reported for a β -keto ether.⁹ For compounds that do not have acetal oxygens, substituent effects suggest a moderately positively charged carbon transition state consistent with an insertion mechanism. When acetals are ozonated, the acetal oxygen stabilizes the positively charged transition state, thereby masking any substituent effects.¹ Small solvent effects and net retention of configuration also support the insertion mechanisms; however, these phenomena could occur with the hydride transfer mechanism if there is a solvent-caged radical pair intermediate. While entropies of activation have been reported to be consistent with both mechanisms,¹ Giamalva et al.⁷ and Nangia and Benson¹² suggest that the experimental values are more consistent with a hydride transfer. The hydride mechanism is also more consistent with the energies of activation for ozonation of C-H bonds than with the insertion mechanism, which requires a highly ordered and energetic pentavalent carbon transition state.^{7,12} Although there is evidence that radicals are present during ozonation, they are not likely to arise from hydrogen abstraction by ozone to form the hydrotrioxides, but result from the decomposition of the hydrotrioxides or other reaction pathways.^{7,12}

Once the hydrotrioxide intermediates are formed, they may decompose either heterolytically (Fig. 2) or homolytically (Fig. 3). The ionic decomposition pathways depend on the other substituents on the hydrotrioxide-bearing carbon, solvents, and other reactants. The products can be either carbonyls and hydrogen peroxide (Fig. 2a), carbonyls and singlet oxygen (Fig. 2b), alcohols and singlet oxygen (Fig. 2c), or carbonyls and alkylperoxy compounds (Fig. 2d).^{3,14} Homolytic cleavage of oxygen-oxygen bonds of the hydrotrioxide can occur at two sites to form either alkylperoxy and hydroxyl radicals (Fig. 3a), or alkoxy and hydroperoxy radicals (Fig. 3b). These radical reactants may then further decompose, abstract a hydrogen, or couple. The radical decomposition reactions may not occur as readily as the ionic

mechanisms in some instances;^{3,14} however, they initiate the formation of radicals that may play an important role in subsequent chain reactions.

Deslongchamps et al. ozonated glycosides,⁴ as well as other acetals,² primarily in nonaqueous solvents. They found that for conformationally rigid glycopyranosides that exist predominately in the C1 conformation, the β -anomers react with ozone while the α -anomers do not. The α -anomers can react with ozone only if they can attain a 1C conformation. The researchers proposed that reactivity with ozone is enhanced in structures with conformations in which a nonbonding orbital of each acetal oxygen is antiperiplanar to the insertion-point hydrogen. Stabilization of a positively charged transition state by correctly oriented nonbonding orbitals is required for the reaction to occur by the proposed 1,3 dipolar insertion mechanism. Either hydrotrioxide or hemioorthoester intermediates may be reaction intermediates. The sole products from ozonated methyl glycopyranosides were glyconate methyl esters. In these studies, the specificity of the decomposition of the intermediate by way of ring cleavage rather than glycoside cleavage was attributed to stereoelectronic requirements similar to those for hydrotrioxide formation. There must be two nonbonded electron pairs antiperiplanar to the departing alkoxy group in the tetrahedral intermediate, a condition which is fulfilled for the cleavage of the ring oxygen, but is not fulfilled for the glycosidic oxygen. Although these reactions by themselves would not result in chain cleavage, the ester linkage would cause the cellulose chains to be susceptible to cleavage by alkaline and acid hydrolysis.

Ozonations of glycosides in aqueous systems have produced different compounds, which suggests there are other significant mechanisms of carbohydrate degradation when water is present. The major products from ozonation of aqueous solutions of β -methyl glycoside are gluconolactone and gluconic acid.⁵ A decomposition pathway for the hydrotrioxide was proposed in which the glycosidic bond is cleaved, rather than the ring oxygen bond, to form gluconolactone, which subsequently hydrolyzes to form gluconic acid. These two β -glycoside reaction mechanisms are illustrated in Fig. 4.

Oxidation of C6 to form glucuronic acid during ozonation of glucose and cellobiose has also been reported.¹⁶ Other products from cellulose ozonation include formaldehyde^{16,17} and glucose oligomers;¹⁶ arabinose is a reaction product as well. Its formation has been attributed to a radical Ruff-type degradation in which the C2 hydrogen of gluconic acid is abstracted, a *gem* diol is formed at C2, and subsequent decarboxylation of C1 occurs. When anomeric mixtures of mannose and xylose were ozonated, similar products were found.¹⁷

Researchers have reported that ozone reacts with α -anomers in aqueous solutions, albeit considerably slower than with β -anomers. Katai and Schuerch¹⁵ proposed a mechanism similar to acid-catalyzed hydrolysis of glycosidic bonds to explain the glucose that resulted as a major product from the ozonation of an α -methyl glucoside. They proposed that ozone directly attacks the glycosidic oxygen to form a tetroxide intermediate, which then decomposes to glucose anomers through a carbocation

intermediate and unspecified degradation products of the tetroxide. The authors felt that the anomeric methyl group was an unlikely site of attack, although other investigators⁷ have shown that methyl ethers react slowly with ozone. Pan et al.⁵ ozonated β -methyl glucoside and also found glucose, but only as a minor product, and proposed the same mechanism.

It is interesting that the methyl ester of gluconic acid was not identified in any of the aqueous reactions of ozone with methyl glycosides, in contrast to the nonaqueous reaction results of Deslongchamps et al.⁴ Possible reasons include a lack of identification of this compound in the reaction mixtures, acid hydrolysis of the ester with a subsequent lactonization of the gluconic acid, or a solvent-mediated shift of the optimal reaction pathway.

Measurements of functional group concentrations in ozonized cellulose from pulp have shown that ozone only moderately increases carboxylic acid groups¹⁸⁻²¹ while carbonyl concentrations tend to fluctuate, but generally increase.¹⁸⁻²⁰ Most of the carbonyl compounds are ketones. While these general trends are similar in most studies, it should be noted that the relative abundances of carbonyl and carboxyl groups vary with different studies. For example, Chirat et al.¹⁸ report carboxyl concentrations ranging from 2.9-3.8 meq/100 g and carbonyl concentrations ranging from 3.2 to 3.8 meq/100 g after ozonating fully bleached pulp (0-0.85% O₃ charge). By contrast, Chandra et al.¹⁹ found higher values, 4.4-4.6 meq carboxyl and 9-23 meq carbonyl/100 g of high cellulose pulp. Godsay and Pearce²⁰ reported values of 0.9 meq COOH/100 g and 2.0 to 4.9 meq carbonyl/100 g of high cellulose pulp (0-10% O₃ charge). These differences illustrate the difficulties in ascertaining the dominant reaction pathways of carbohydrate degradation. The equilibrium between chain esters, lactones, and acids, coupled with the analytical difficulty in differentiating the carbonyl functional groups in complex mixtures, makes elucidation of the direct mechanism of ozone degradation of cellulose challenging.

The introduction of carbonyl groups seriously affects the stability of carbohydrates in alkaline conditions, as well as color reversion. Carbonyl groups at C2 and C3, have been implicated in the susceptibility of ozonated pulp to degradation by β -elimination reactions during alkaline extraction stages. The low apparent viscosity of ozonated pulps, relative to strength properties, has also been attributed to carbonyl groups produced by ozone; depolymerization reactions occur during the alkaline viscosity assay. By contrast, oxidation of C1 and C6 to acid groups imparts a resistance to hydrolysis for carbohydrates and inhibits further degradation. Reduction of carbonyl groups to alcoholic groups also retards carbohydrate degradation by ozone.

Reactions With Lignin

The strong electrophilic properties of ozone allow it to react efficiently and rapidly with sites of high electron densities in lignin, such as double bonds in the side chain and the aromatic rings. In addition, ozone may also attack the C-H bonds in aryl ether substituted side chains. Reactions of ozone with lignin are complex because of the diversity of potential sites of attack and because products of the initial attack are quite susceptible to further attack. Furthermore, other reaction byproducts, such as hydrogen peroxide, are also reactive.

Reactions of ozone with alkenes proceed by way of the Criegee mechanism (Fig. 5). The reaction begins with a 1,3 dipolar concerted addition reaction across the double bond to form a highly unstable 1,2,3-trioxolane, or primary ozonide (Fig. 5a). Although the primary ozonide may directly decompose into a carbonyl and hydroperoxide by attack of participating solvents (Fig. 5b), it is more likely to cleave at the C-C bond to produce a carbonyl and a carbonyl oxide zwitterion or radical pair (Fig. 5c). The directionality of the cleavage depends on the carbocation or radical stabilization capabilities of the substituents on each of the alkenyl carbons; thus, a higher degree of alkyl substitution on a carbon allows it to become the carbonyl oxide. Once the two fragments are formed, several pathways are possible.

For aldehydic carbonyl compounds in inert solvents, the two fragments may recombine to form 1,2,4-trioxolane, or a secondary ozonide (Fig. 5d), which can be readily isolated in many cases. When the secondary ozonide is exposed to water, it can hydrolyze to two carbonyl fragments and hydrogen peroxide, probably through a hydrotrioxide intermediate (Fig. 5e). Alternatively, it may decompose to a carboxylic acid and a carbonyl compound (Fig. 5f). In addition to recombining with the carbonyl compound, the carbonyl oxide can also undergo dimerization reactions to form bisperoxides.

Decomposition of the primary ozonide to the carbonyl and carbonyl oxide fragments is the reaction pathway that is most likely to predominate in the aqueous conditions normally used in ozone bleaching. The carbonyl oxide is trapped by water to form an α -hydroxy hydroperoxide (Fig. 5g). The fate of the hydroperoxide depends on other substituents and solvents. The hydroxy group, originally from the water, can become a carbonyl group, releasing hydrogen peroxide (Fig. 5e). Under acidic conditions, the peroxy oxygen can become protonated, forming hydrogen peroxide and a carbocation. The carbocation then reacts with water to form a *gem* diol that is likely to become further oxidized to a carbonyl compound (Fig. 5h). Also in acid, the terminal oxygen in the peroxy group can become protonated. If there is a group on the carbon that migrates easily, a rearrangement can occur to form a carbonyl and an alcohol (Fig. 5i). Finally, if one of the groups on the hydroxy hydroperoxide carbon is hydrogen, the peroxide can decompose to water and a carboxylic acid (Fig. 5j).

Aromatic compounds also react by the Criegee mechanism, although at a slower rate than alkenes. There are three sites of attack on each aromatic ring. Preferential sites of attack and higher

rates of reaction will occur at those carbons with the highest electron density. Therefore, aromatic compounds with the most electron-releasing groups react most rapidly with ozone, and the ozonide forms at the carbons bearing the electron-releasing groups. Once the ring cleavage product is formed, a muconic acid, the two aliphatic double bonds also become susceptible to attack.

At least three other reaction pathways have been proposed for aromatic compounds, particularly phenols. Phenols become hydroxylated, and quinones have been reported as ozonation products. Standard electrophilic substitution mechanisms have been invoked to explain these products.^{22,23} The electron deficient ozone oxygen attacks the aromatic pi electrons; an arenium ion forms that, for the ozone electrophile, is a trioxide carbocation. The trioxide anion loses oxygen and the ring either rearomatizes so that the net result is ring hydroxylation, or quinones form if good leaving groups are present. Epoxidation can also occur via electrophilic substitution at double bonds.^{24,25} Hydrogen abstraction from phenolic hydrogens has also been proposed as an initiating reaction for the formation of quinones, and for polymerization reactions in nonaqueous solvents.²⁶

Nearly all of these reactions have been reported for the ozonolysis of lignin model compounds and lignin. Common pathways of ozonolysis proposed for lignin-type compounds are summarized in Fig. 6, which shows the complete oxidation of all unsaturated sites in an aromatic model. Ozonides, isolated from veratryl lignin model compounds ozonated in inert solvents, decompose to small aldehydes, acids, and methyl esters upon warming.²⁷ Lignin model dimers give similar small, oxygenated products as well as monomeric rings. Quinones and other "active oxygen" compounds have been reported as ozonation products of lignin and lignin model compounds.^{27,28} The mechanisms discussed previously were used to explain the reaction products.

Most of the differences in reactivity between functional groups in lignin can be explained in terms of an initial reaction that is strongly electrophilic; the most electron-donating substituents enhance reactivity, while electron-withdrawing substituents inhibit it. These combined reactivity phenomena lead to interesting competitive pathways of ozone consumption. Eriksson and Gierer²⁴ report that the order of ozone reactivity of lignin models is stilbenes > styrenes > phenols > muconic acids > nonphenols > aldehydes. Therefore, ozone will cleave the double bonds in stilbenes and styrenes before attacking any aromatic rings. Such reactions are likely to be important for delignification and for decolorization²⁹ of kraft residual lignin which is enriched in vinyl ethers compared to wood lignin. Once the side chain double bonds are cleaved, the aromatic rings are attacked. Phenolic lignin models react with ozone before nonphenolic lignin models; this is probably related to the electronic effects of the hydroxyl and methoxyl groups (e.g., Hammett constants σ_p for -OH and -OCH₃ are -0.38 and -0.28, respectively). Other substituents, of course, will also have an impact. Kojima et al.³⁰ attributed the reactivity of dimeric model compounds toward ozone to the total number of substituents on the two rings. Thus, a guaiacyl biphenyl (2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dialkyl diphenyl) with a total of 8 activating ring substituents reacted

faster than phenylcoumaran with a total of 7 groups (3 alkyl, 2 methoxyl, 1 alkoxy, 1 hydroxyl), which, in turn, reacted faster than a β -aryl ether with a total of 5 alkoxy or alkyl ring substituents. Furthermore, when dimeric compounds are ozonated, the ring with the most activation will react first; many times it will be the only ring that reacts, but not always.³¹

As with any electrophilic reactions, substituents will help direct lignin reaction pathways. For example, model compound work has shown that aromatic ring cleavage will occur primarily (but not exclusively³¹) between oxygen-bearing C3 and C4 for softwood lignin models that have an electron-donating side chain. However, if the side chain is electron withdrawing, rates of ozonation decrease and cleavage increases at C2-C3 or C4-C5, producing more nonesterified small acids.²⁷

The products of the initial ring attack, muconic acid derivatives, have opposing reactivity features: they are olefins, which promotes their reactivity over the parent aromatic, but they also have electron-withdrawing carbonyl groups as a result of the oxidation. These characteristics make the reactivity of muconic acid structures to ozone generally intermediate to phenolic and methoxylic aromatic compounds. Therefore, once ring cleavage occurs in dimeric compounds, if the remaining ring is phenolic, the second ring will be attacked. Conversely, if the second ring is methoxylic, the side chain will continue to be attacked by ozone and the second ring will remain intact.²⁴ Ozonolysis of the two double bonds in muconic acid structures produce the two-carbon oxygenated fragments typically found in lignin and lignin model ozonations, including glyoxal, glyoxilic acid, glyoxilic acid methyl ester, oxalic acid, monomethyl oxalate, and dimethyl oxalate. The primary pathways to these products from lignin phenolic monomers is given in Fig. 6. For the phenylpropane monomer shown, four moles of hydrogen peroxide can be generated, along with two moles of glyoxilic acid, one mole of glyoxylic acid methyl ester, one mole of formaldehyde, and one side chain carbonyl functional group, when the unsaturated sites are fully oxidized.

Under limiting ozone conditions, muconic acid derivatives may form lactones, rather than cleaving to smaller products. If there is an α -hydroxyl group on the side chain, the oxygen will bond with the C4-carbonyl carbon to form a δ -lactone for both phenolic and nonphenolic compounds.^{30,31} If an α -hydroxyl group is not present on the side chain, a γ -lactone will form between C1 and the carboxylate oxygen of an oxidized phenolic at C4.²⁴

The predominate pathways of lignin model ozonolysis are those that have been discussed. However, the potency of ozone and the complexity of both lignin and its reaction byproducts allow numerous other reactions to occur. The prevalence of one pathway over another depends on the reaction conditions and the specific features of the lignin. For example, while it appears that most hydroperoxide intermediates decompose by losing hydrogen peroxide, rearrangements may also occur.^{27,28} In another pathway, hydroperoxides decompose to produce the carboxylic acids that are prevalent in ozone mixtures. However, it is difficult to differentiate the latter pathway from a simple oxidation of aldehydes to acids. Substitution reactions may produce epoxides from muconic acid derivatives,²⁴ hydroxylate

phenols,³¹ and produce quinones.²⁸ The formation of high molecular weight material from ozonation of lignin model compounds indicates that ozone can initiate polymerization; Diels-Alder type reactions, radical coupling, and esterification have all been proposed as potential routes.^{31,32}

Balousek et al.³¹ ozonated a β -aryl ether model compound and found products that supported a reaction in which the ozone inserts into the β -carbon-hydrogen bond, forming a hydrotrioxide intermediate, similar to the reactions with glycosides discussed previously. They proposed a homolytic decomposition pathway to a hydroperoxy radical and a ketone, analogous to a mechanism reported by Plesnicar et al.¹⁴ for α -methyl benzyl ethers and alcohols. It is noteworthy that the insertion reaction was competitive with the rapid reactions with electron-rich alkenes and aromatics; it might be predicted to have a considerably slower reaction rate. However, if the lignin insertion reaction occurs under bleaching conditions, it is likely to effectively depolymerize the portions of the residual lignin macromolecule that still retain β -aryl ethers after cooking.

Many of the reactions that have been proposed as a result of model compound studies have been borne out by changes in the concentrations of functional groups when lignin and pulp are exposed to ozone. There is a pronounced increase in carboxylic acids in lignin in residual lignin of ozonated kraft pulp,^{18,21} dissolved lignin fragments from ozonated kraft pulp,²⁸ as well as ozonation products of isolated wood lignins,^{28,33} and isolated kraft lignin.^{27,34} Carbonyl groups also increase in number with ozonations,^{18,28,29,34} although the extent is variable and limited.

As expected, ozone depletes phenolic groups in kraft residual lignin,^{18,21,34} similar to oxygen and chlorine dioxide.³⁵ The aromatic content of ozonated wood lignins is less than that of unozonated lignins.^{28,33,36} However, the reactivity of wood lignin appears to be different from kraft residual lignin. Chirat and Lachenal¹⁸ found the aromatic carbon content of residual lignin from ozonated kraft pulp to be similar to the original residual lignin. The latter result suggests that most ring cleavages that occur during ozone bleaching of kraft pulp ultimately cause dissolution of the lignin. This may be a function of the competitive nature of the muconic acid reactions versus the aromatic reactions. Such a conclusion is supported by the fact that molecular weight distributions of residual lignin of ozonated pulp are not substantially changed by moderate charges of ozone.^{34,35} Furthermore, analyses of the dissolved fragments from ozonated pulp and groundwood show little intact aromatic compounds^{28,37} and there appears to be more high molecular weight material in filtrates from ozonated pulp than from pulps treated with other bleaching reagents.^{38,39} Together, the data suggest that the biggest impact of ozone on kraft lignin is the introduction of hydrophilic groups rather than substantial depolymerization.³⁵

Methoxyl and methyl ester contents are somewhat variable for ozonated pulp, and the values depend on the substrate, conditions of ozonation, and the analytical methods used. Demethoxylation may arise from ester hydrolysis of cleaved rings, or from a radical demethoxylation pathway, both of which are likely to be highly dependent on the pH, metals content, and other variables of the reaction medium.

Freshly ozonated lignin appears to contain reactive intermediates that degrade over time. It has been suggested that this "active oxygen" consists of hydroperoxides, peroxides, ozonides, or quinones.^{28,40} There is also evidence of free radicals in ozonated lignin mixtures,⁴⁰ and they may cause polymerization or other radical-initiated reactions.

Selectivity

Selectivity refers to the preferential attack of a reagent on lignin versus carbohydrates. The rates of carbohydrate reactions determine selectivity under various ozone bleaching conditions. Carbohydrates may react with ozone directly, or react with lignin or carbohydrate byproducts, particularly radicals. Radicals, in turn, may be initiated from the decomposition of ozone, byproduct hydrogen peroxide, hydroperoxidic lignin byproducts, or intermediate hydrotrioxides. The contribution of each of these pathways of carbohydrate deterioration is currently unclear due to contradictory conclusions from numerous studies (e.g., references 41-44). When these processes are better understood, it may be possible to develop strategies to effectively prevent or minimize the most important pathways of carbohydrate deterioration. Furthermore, a clearer understanding of the maximum possible selectivity of ozone bleaching will be gained.

Direct Reactions

Selectivity depends, in part, on the reactivity of ozone directly with various functional groups. Second order rate constants for direct reactions of ozone with several compounds that have functional groups relevant to pulp are given in Table 1. These rate constants and other kinetic parameters suggest that when lignin is present, ozone should be rapidly consumed by the lignin and cellulose should be fairly unreacted.

The data in Table 1 indicate that the double bond of styrene and the activated benzene rings are very reactive, followed by the aliphatic unsaturated acids. Only the very small acids react more slowly than the carbohydrates. The data suggest that carbohydrates are protected from direct reactions with ozone by the presence of lignin and lignin degradation products. There is considerable data supporting this contention. Even benzaldehyde, a deactivated lignin structure, completely degrades before β -methyl glucopyranoside begins decomposing in ozonated mixtures.²⁴ Guaiacol and syringol are nearly

completely consumed before the β -glucoside is degraded when mixtures of the compounds are ozonated.⁵

The model reactivities are reflected in pulp ozonation. When initial kappa numbers of pulp are high, viscosity is retained better than when ozonation occurs in later stages of a bleaching sequence and the initial kappa numbers are low.^{21,45,46} Once a critical level of lignin has been removed from the pulp, ozone will begin to react to a greater extent with the C-H bonds of carbohydrates. The protecting effect of lignin appears to exist only to a point; at lower kappa numbers, lignin appears to promote carbohydrate degradation.^{46,47} It has been suggested that ozone may abstract phenolic hydrogen atoms which initiates a radical pathway that forms the hydroxyl radical.⁴⁸ This may explain the superior selectivity of oxygen bleached pulps over kraft pulps because oxygen preferentially depletes phenolic structures in residual lignin.⁴⁴

Radical Reactions

There are numerous species of radicals that may be associated with the ozonation of organic compounds in aqueous conditions. These radicals are involved in complex initiation, propagation, and termination reactions that depend upon several reaction parameters. The pH, time, inorganic and organic substrates, as well as other reaction conditions can have a strong impact on the formation of radicals and the mechanisms by which they are destroyed.

The hydroxyl radical is clearly an important radical species that is formed directly from decomposition of ozone or reaction intermediates, or from chain reactions initiated by other radicals. The selectivity factor of the hydroxyl radical for lignin over carbohydrates is substantially lower than for the direct ozone reactions.⁴⁹ For this reason, the hydroxyl radical is often invoked as the species that is responsible for carbohydrate deterioration. Other species that may be formed include hydroperoxyl ($\text{HOO}\bullet$), organic peroxy ($\text{ROO}\bullet$), organic oxyl ($\text{RO}\bullet$), and ozonide ($\text{HOOO}\bullet$) radicals. While these latter compounds are less reactive than the hydroxyl radical,⁵⁰ they enter into complex chain reactions that may ultimately produce hydroxyl radicals.

During ozone bleaching, it is possible that radicals may form directly from ozone or they may arise from the homolytic decomposition of products from direct ozone reactions. The main pathways include metal-catalyzed decomposition of ozone, homolytic decomposition of lignin peroxides, metal-catalyzed decomposition of intermediate hydrogen peroxide, and hydrogen abstraction by ozone followed by decomposition of the resulting hydrotrioxide. Another potential source of radical initiation is the

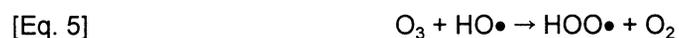
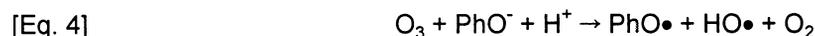
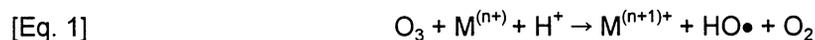
decomposition of the hydrotrioxide intermediates of carbohydrates and lignin. These pathways are briefly reviewed.

Radicals from Ozone Reactions

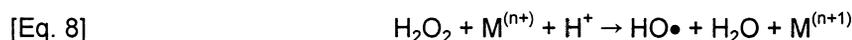
The decomposition of ozone to radicals is initiated by hydroxide ions and metals. Other pathways that produce radicals directly from ozone are reactions with other radicals and abstraction reactions. Under the acidic conditions used in pulp bleaching, the ozone reactions that are most likely to directly initiate radical formation are the metal-catalyzed decompositions [Eq. 1] and hydrogen abstraction reactions [Eq. 2-4]. Radical chain reactions [Eq. 5-7] will consume more ozone and propagate more radicals. The radicals will exist predominately in their protonated form under typical bleaching conditions (pKa of HOO• = 4.9); however, low levels of the superoxide radical anion are likely to be present even at low pHs and may be sufficient to propagate radical pathways.^{48,51} Many of the reactions proceed through ozonide intermediates.

Protonated phenols probably react primarily by nonradical mechanisms because of the rapidity of those reactions; however, as shown in Eq. 4, abstraction of an electron by ozone from phenolates may be a source of radicals.^{48,51} This pathway is probably only significant when the pH of the bleaching conditions is above 3 and the proportion of ionized phenols is sufficient for the reaction to take place. Below pH 3, phenols with an α -carbonyl group may react by the abstraction pathway because of their reduced pKa.⁵¹

It has been suggested that a key radical intermediate is the superoxide radical anion that propagates hydroxyl radical formation by its reactions with ozone [Eq. 7], as well as reactions with hydrogen peroxide.⁵¹ The superoxide arises from the decomposition of organic peroxy radicals. It has been proposed that by controlling the level of the superoxide radical anion, the radical chain reactions may be terminated, and selectivity improved.⁵¹



Another source of radicals is the decomposition of peroxide and hydrotrioxide intermediates produced from direct ozone reactions. Hydrogen peroxide arises primarily from the decomposition of hydroxy hydroperoxide intermediates of lignin (Figs. 5e and 6). A comparatively minor source is the homolytic decomposition of hydrotrioxides (Fig. 3b). The main radical initiation mechanism from hydrogen peroxide is the classic, metal-catalyzed Fenton reaction [Eq. 8]. High concentrations of H₂O₂ during high consistency bleaching may cause this pathway to be more important than at low consistency conditions.⁵² Hydrogen peroxide may also propagate radicals by reacting with superoxide radical anions to form the highly reactive hydroxyl radical [Eq. 9].⁵¹ Although ozone will react with H₂O₂ at a high pH, the reaction is suppressed at low pH,⁵³ and probably is not a significant pathway for radical production during ozone bleaching.



Organic peroxides are most likely to arise from reactions of ozone with lignin (Fig. 5g). They may decompose to radicals by direct reactions with ozone [Eq. 3] or by metal-catalyzed reactions [Eq. 10-11]. Propagation reactions in which the peroxides are involved include the abstraction of hydrogen from the peroxides by alkyl radicals [Eq. 12-13]. Peroxyl and alkoxy radicals participate in additional chain carrier reactions [Eq. 14-16]. Equation 14 may be particularly important because it represents another pathway to the superoxide radical anion, a proposed key radical chain carrier.^{48,51} Note that under oxygenated conditions, an additional pathway to peroxyl radicals may be coupling of oxygen to organic radicals [Eq. 17].



Hydrotrioxides may arise from ozone insertion in C-H bonds in carbohydrates (Fig. 4) and in the side chains of lignin. Although these reactions are expected to be slow compared to other ozone reactions, they may play a part in the radical initiation under some conditions.⁵⁴ Numerous homolytic decomposition of hydrotrioxides are outlined in Fig. 3. The types of radicals formed are comparable to those already discussed ($R\bullet$, $RO\bullet$, $ROO\bullet$, $HO\bullet$) and enter into the same propagation reactions.

Hydroxyl Radical Reactions

Reactions of lignin with the hydroxyl radical are only marginally favored over carbohydrate reactions ($k_{\text{lignin}}/k_{\text{carbohydrates}} = 5-6$).⁴⁹ Hydroxyl radicals react readily with lignin in pulps with high lignin content; although at least one study indicates there is little delignification due to these reactions.⁴³ Model compound studies with hydroxyl radicals and lignin show that phenols and etherified phenols react differently. Radical coupling predominates when phenols are exposed to hydroxyl radicals, while hydroxylation and demethoxylation are the major reactions with etherified phenols.⁴¹

Hydroxyl radicals may react with carbohydrates by abstracting hydrogen atoms from either C1 or C2.^{52,55} The resulting radicals may couple with oxygen to form intermediate organic peroxy radicals. Depolymerization might occur as a direct result of fragmentation of the intermediate radicals. Alternatively, if carbonyl groups are introduced at C2 as a result of hydrogen abstraction and oxygen coupling at C2, then depolymerization may take place through β -elimination when the carbohydrates are exposed to alkaline conditions.⁵⁵

Mass Transfer Limitations

Because of its high reactivity, ozone mass transfer to lignin is critical during ozone bleaching. Diffusion of ozone across the immobile water layer adjacent to the cell wall can be a significant rate-determining step for low consistency and poorly mixed medium consistency bleaching.⁵⁶ Diffusion within the cell wall is rate limiting in high consistency and well-mixed low consistency ozone delignification. Griffin et al.⁵⁷ have proposed a model of ozone delignification whereby an advancing front of lignin-ozone

reactions takes place across the cell wall to the lumen. They propose that the highly reactive hydroxyl radicals produced by ozone-lignin reactions immediately degrade the adjacent carbohydrates, and therefore, all cellulose decomposition takes place within the ozone-lignin front.

APPLICATIONS

When ozone is applied to pulp, several process conditions must be optimized to maximize the desired reactions with lignin and minimize the harmful reactions with carbohydrates. Optimizing efficiency and selectivity generally focuses on: 1) minimizing ozone decomposition, 2) promoting uniform exposure of lignin to ozone, 3) minimizing exposure of carbohydrates to radicals and high ozone concentrations, and 4) minimizing reactions of ozone with dissolved byproducts. Important controlling parameters are consistency, charge, pH, concentration of ozone in the gas, time, temperature, carry-over, metals removal, mixing, additives, and position in sequences.

In general, ozone decomposition is reduced at conditions of low pH, medium or high consistency, effective metals removal, low charges, and low temperatures. Uniform bleaching is promoted by effective mixing and fluffing (at high consistency). Carbohydrates are protected from high ozone concentrations by using charges less than 0.5% by weight and by good mixing. Viscosity is sometimes better preserved at low and well-mixed medium consistency and by shorter reaction times. Exposure of cellulose to radicals can be reduced by additives that act as radical scavengers as well as by reducing ozone decomposition.

Bleaching efficiency can be reduced by carry-over; for example, a COD load of 10 kg COD/ADt was found to double the ozone demand in medium consistency pilot trials.⁵⁸ Lower kappa number pulps are generally considered suitable for ozone bleaching because of the relatively high cost of ozone. Oxygen delignification is often used prior to a Z stage because of the low expense of oxygen and because the residual lignin remaining from oxygen appears to react readily with ozone.

Excellent and extensive reviews of industrial applications of ozone bleaching have recently been published.⁵⁹⁻⁶¹ Important process variables in ozone bleaching and their impact on selectivity and efficiency are briefly reviewed below.

Consistency

Early work on consistency showed high consistency produced the strongest pulps. However, as mixing technology has improved, results at low and medium consistency have improved. All three conditions have been used and each has its disadvantages. Low consistency disadvantages include a large water demand, large effluent volume, and mixing limitations. In medium consistency, the gas-to-pulp ratio must be small enough to be adequately mixed, yet the ozone concentration must be high enough to delignify. Either the O₂/O₃ stream must be pressurized or a high concentration of ozone in the O₂/O₃ flow must be used; each option has its drawbacks.

Lindholm^{62,63} found that low consistency is more selective than high consistency, which was attributed to better homogeneity at low consistency. Carbohydrates may degrade more during high consistency bleaching because of the heterogeneity of the system, which causes localized areas of high ozone concentration and low lignin concentration. During low consistency bleaching, the reaction medium is more homogeneous, the ozone can be more readily dispersed, and reaction products may contribute to carbohydrate-protecting effects.⁶⁴ In medium consistency pilot studies, selectivity was between that of high and low consistency.⁵⁸ However, lab results show best selectivity at medium consistency with high intensity mixing.^{65,66}

Delignification efficiency (the amount of ozone required per unit kappa number drop) has been found to be worst at low consistency in lab studies,^{63,66-68} although one study reported delignification efficiency to be unaffected by consistency.⁶⁵ More ozone is consumed at lower consistencies.^{63,66} Since the consumed ozone does not result in more delignification, more decomposition or secondary reactions must occur at the lower consistencies. The combination of improved delignification at high consistency and improved viscosity retention at low consistency has driven the interest in medium consistency ozonation.

Charge and pH

Increasing the charge of ozone from 1-2% by weight decreases the kappa number and increases the brightness at the expense of viscosity. Without a cellulose protector, a 1% charge of ozone has been considered to be the maximum for optimal cellulose quality.^{67,69} In practice, ozone charges generally do not exceed 0.7%, even for softwoods, which require higher charges.

A pH between 2 and 3 is optimal for pulp ozonation.^{58,63,67} Delignification is improved at low pH, and the strong acidity does not contribute to substantial losses of viscosity. Viscosity loss is minimal up to

pH 4. Beyond pH 4, viscosity loss occurs and brightness is reduced.⁵⁸ Low pH may be optimal because of three factors. Decomposition reactions that produce radicals are inhibited; metals that promote ozone decomposition may be removed in acid washes; and primary ozone-lignin reactions may be favored.⁶³ The dependency of delignification on pH has been found to be more complicated when pulps have a higher residual lignin content.⁴⁶ Furthermore, recent work suggests that high pHs can be tolerated during ozone bleaching under appropriate conditions.⁴³

Concentration

The concentration of ozone produced in O₂/O₃ streams is important because it affects pulp quality and because it affects the optimization of various other process variables, particularly reaction time. In general, concentrations below 10% have been used due to safety considerations and limitations on ozone generation. More recently higher ozone concentrations up to 15% have been effectively employed (e.g., reference 70).

The dependency of pulp quality on concentrations of ozone varies depending on whether very low concentrations are used (<3%) or higher concentrations are used (10%). When increasing the concentration up to 2-3% by weight, lower concentrations improved viscosity using high consistency conditions.⁶⁸ However, a 10% concentration was found to be more selective than a 2.2% concentration, also using high consistency; the higher ozone concentrations resulted in greater delignification.⁷¹ Medium consistency ozonations are also more selective at higher ozone concentrations.⁵⁸ Other researchers have found little effect of ozone concentration on kappa number or viscosity,^{59,60,72} but higher concentrations reduced reaction times for delignification.^{59,60}

Time

Reaction time is particularly important at low and medium consistencies. When constant ozone charges have been applied to softwood pulps at different reaction times, longer reaction times resulted in higher ozone consumption and improved delignification for low and medium consistency ozonations. With long enough reaction times, delignification at low and medium consistency nearly matched that achieved under high consistency conditions.⁶⁵ At high consistency, longer reaction times suppress carbohydrate degradation but do not affect the drop in kappa number.⁶⁸

Hardwood pulps appear to have a different time dependency than softwoods. Laboratory experiments using medium consistency showed that hardwood pulp ozone consumption increases with reaction times, but brightness and delignification actually decrease.⁶⁵ Pilot studies using medium consistency ozone bleaching of hardwood dissolving pulp also found that longer reaction times consume more ozone with no increase in delignification.⁵⁸

Selectivity is best in the beginning of high consistency ozone bleaching and drops off later.^{21,71} Increases in the concentrations of radicals or radical precursors, coupled with a decrease in the amount of available lignin to consume the radicals, are possible reasons for this observation.

It is important to note that the dependence of bleaching behavior on reaction time may be a significant variable in comparing some laboratory studies to mill practices. While laboratory studies generally employ reasonably long reaction times, technical bleaching may be conducted in seconds (medium consistency) or minutes (high consistency).

Temperature

Lower temperatures promote selectivity probably by reducing carbohydrate reactions.⁷³ High temperatures promote ozone decomposition, which creates the cellulose-degrading radicals, although below 25°C, ozone decomposition is minimal.⁷⁴ Delignification is fairly constant up to about 55°C for medium consistency hardwood ozonation; kappa numbers rise slightly at higher temperatures.⁵⁸ Liebergott et al.^{60,61} reported slight increases in kappa and slight reductions in viscosity when temperatures were raised from about 20 to 80°C. These effects have been attributed to increased ozone decomposition with temperature. For low consistency operations, temperature will also affect ozone solubility, which may, in turn, affect bleaching efficiency.⁷⁵

Carry-over/Filtrates

The effects on ozone efficiency of carry-over and of dissolved organic material in filtrates are important because of the implications for brownstock washing and filtrate recycle, respectively. Although ozone reacts with organic material in ozonation filtrates, Lindholm and Vilpponen⁷⁶ found that it will react with pulp preferentially. Consequently, ozonating pulp using recycled ozonation filtrates at high or low consistency does not affect delignification efficiency. In fact, viscosity protection at low consistency has

been attributed partly to the presence of degradation products.⁶⁴ By contrast, a COD carry-over load of 10 kg C/ADt was found to double the ozone demand in medium consistency pilot trials.⁵⁸

Mixing

Doubling mixing times reduced kappa numbers and increased efficiency in the medium consistency ozonation of hardwood pulps.⁵⁸ Increasing mixing intensity improved viscosity protection and delignification (when adequate reaction times were used) in medium consistency bleaching.⁶⁵ There is higher ozone consumption at higher mixer speeds when ozonating at medium consistency. As the ZE stage (after ozone and alkaline extraction) brightness increases, viscosity and lignin levels decrease with increasing mixer intensity for softwoods and hardwoods.⁶⁵

Additives/Solvents

Large numbers and types of compounds have been evaluated for their potential as carbohydrate protectors and have been compiled by Liebergott et al.^{59,60,67} Nothing that is commercially feasible has been found to be highly effective and Liebergott notes that the problem of finding an inexpensive effective commercial inhibitor of carbohydrate depolymerization during ozone delignification remains to be solved.⁶⁷

Methanol has been found to protect cellulose; DMSO protected carbohydrates at high consistency without inhibiting delignification in one set of studies,⁶⁸ but another study found no effect of DMSO at high consistency or low consistency.⁶⁴ It is interesting that some chemicals that protect cellulose in oxygen bleaching do not work with ozone, which suggests that some carbohydrate damage from ozonation does not arise from radicals.

The acids used to reduce pH may affect ozone efficiency. Although acetic acid inhibits metal-catalyzed decomposition of ozone, some studies have shown that there is no difference between sulfuric acid and acetic acid (at low consistency) on viscosity, strength,⁶⁸ or delignification efficiency.⁶⁴ More recent studies suggest that ozonating in 90% acetic acid under low consistency conditions improves selectivity, particularly when ozonating down to low kappa numbers.^{44,77} Oxalic acid also improves selectivity at low and high consistencies at a pH <2.⁶⁴

The protective effects of lignin and lignin fragments have been noted^{64,77-79} and attributed to radical scavenging by these materials.⁴⁶ On the other hand, cellulose reacts with ozone more readily in

the presence of small amounts of lignin than under lignin-free conditions, which may result from cellulose attack by radical intermediates generated by lignin oxidation.^{46,47}

Sequences

Placement of an ozone stage in several different points in a bleach sequence have been investigated over the years. Most bleaching sequences now use an oxygen stage prior to ozonation and place the ozone stage early in the sequence. Examples of sequences recently implemented in pilot plants include OZP (Graz, Austria), OZEP (Baienfurt, Germany), OZEP, OZED, O(pZE)P (Paprican), and (O)Z with any sequence (Espanola, Ontario). Two recent commercial installations have employed (EOP)ZP (Lenzing, Austria) and OZ(EO)D or OZEP (Franklin, VA). Sequences such as ZPZP, ZEP, chelation followed by OO(ZE)P(ZE)P, OO(ZE)PP, ZEDED, and others have also been studied.

Comparison of the different positions of ozone in a bleaching sequence is influenced by the position of alkaline extraction stages. The carbonyls formed from cellulose ozonation are susceptible to further reaction under alkaline conditions, resulting in depolymerization and viscosity reduction. Some studies show that ozone selectivity is lost in an alkaline post-treatment stage,^{46,71} resulting in a recommendation that ozone be introduced last or that a strong reducing agent be added to the alkali stage. Other studies show inconsistent or negligible effects on viscosity at charges of 1% ozone or below and 1 to 1.5% NaOH charge in the extraction stage.^{59,60,65} Lachenal et al.^{78,79} have noted that although ZE produces pulp with lower viscosity than Z, the latter is still better than an O stage at low kappas. Alkaline extraction reduced brightness when comparing an OZD to an OZED sequence.^{59,60}

Washing between Z and E stages resulted in slightly higher kappas than when there was no washing between Z and E.⁶⁷ Washing between a D stage and a Z stage was also found to be unnecessary.^{78,79}

Generally, oxygen bleaching prior to ozone application is better than the reverse sequence.^{59,60,71,78,79} Because ozone does not react well with bark and shives, better quality pulp results when oxygen precedes ozone. Also, it is economically more feasible to use oxygen to remove the bulk of lignin and to follow up with ozone. A peroxide stage between an O stage and a Z stage has been shown to improve pulp bleachability.⁶⁸

Ozone has been used to replace chlorine, chlorine dioxide, or hypochlorite stages in traditional sequences. Using a chlorine dioxide stage immediately adjacent to an ozone stage to achieve a constant kappa number improves selectivity over ozone alone. The high selectivity of chlorine dioxide is utilized in this sequence. Furthermore, a DZ sequence results in a higher viscosity pulp than a ZD sequence.^{78,79}

Two possible reasons have been put forth. In a DZ sequence, the chlorine dioxide may modify the residual lignin so that lignin becomes more reactive to ozone. Alternatively, a DZ sequence may result in fewer cellulose-degrading radicals arising from lignin oxidation, thereby reducing carbohydrate degradation from that source. An O(DZ)ED sequence produced good viscosity pulp with a very low AOX in effluent.^{78,79} Hypochlorite or ozone followed by peroxide resulted in similar viscosity losses in medium consistency bleaching.⁵⁸ However, when one D stage is replaced by ozone in a DEDED sequence, the brightness ceiling is lowered.⁴⁶

ENVIRONMENTAL BENEFITS

The environmental effects of wastewaters from oxygen-based bleaching, relative to those from chlorine-based bleaching, vary due to the influence of a number of factors. Some of these include differences in wood species, quality of pulp produced, the extent and specifics of water recycling, target species for toxicity assays, other bleaching stages used, the receiving water quality, and even the specific experimental techniques used (including sample preservation and storage). It is also important to recognize that the bleach plant is only one input into whole mill effluents; dilution and chemical transformations will take place. Furthermore, the ultimate environmental loading from a mill will depend on the effectiveness of biological treatment, which varies from site to site.

Despite the variability, it is clear that replacing a C or D stage with ozone drastically reduces the formation of AOX and specific chlorinated compounds. While effluent AOX ranges from 0.1 to 1.0 kg ptp for mills using chlorine dioxide without oxygen,⁸⁰ some values reported for AOX from ozone bleaching filtrates include nondetect for a (QZ)(Q)(PO) mill sequence,⁸¹ 0.0002 kg/tonne for a Z(PO) laboratory sequence,⁸² and 0.09 kg/ADMT (D filtrate) from a mill OZED sequence.⁸³ The actual benefit to the environment from low AOX discharges is unresolved. In general, at discharges less than 2 kg/ton, AOX does not correlate with toxicity or other environmental effects, while discharges above 2 kg AOX/ton do correlate with environmental impacts.⁸⁰ Chlorodioxins, chlorofurans, and chlorophenols, which can have a significant environmental impact, are not detected; however, traces of chloroform remain in some TCF cases.⁸³ A potentially significant environmental advantage to TCF bleaching is the expected decline in the releases of chlorine and chlorine dioxide, two important Toxics Release Inventory chemicals. It is unclear how emissions of other volatile compounds from the bleach plants using TCF and ECF sequences differ.

The oxygen demand parameters in effluents will vary considerably depending on how much lignin and carbohydrates are removed from the pulp in the bleach plant, and on how much water is recycled back to recovery. An OZED sequence with nearly complete recycle of the OZE stages produces mill

discharges of COD and BOD that are at least 90% less than discharges from a CEDED sequence and 70-90% less than an O(DC)ED sequence.⁸⁴ No water recycle with OZED sequences results in comparable or slightly higher levels of organic carbon,⁸⁵ possibly due to larger quantities of carbohydrates in TCF filtrates than in ECF filtrates. Laboratory studies in which TOC, COD, and BOD have been measured in untreated and treated filtrates suggest that the organic material produced in ozone-containing sequences is more easily degraded by microbes than ECF filtrates.⁸² These findings are consistent with the higher BOD/COD ratios of wastewaters containing ozone filtrates than for wastewaters with C or D stage filtrates.^{82,86}

The toxicity of ozone filtrates has been found to be higher, lower, and the same as conventional filtrates, depending on the specific study. For example, exposure of several marine organisms to untreated filtrates from D(EO)DD and Z(PO) sequences (using 50 and 22 m³ water/tonne pulp, respectively) showed that ozone filtrates were generally more toxic than the untreated D filtrates.⁸² Target organisms included scallops, algae, urchins, fish, and bacteria. Peroxides in the untreated ozone filtrates may have been a primary source of toxicity in the TCF filtrates. Similarly, laboratory Z filtrates in a TCF sequence had a higher chronic toxicity to fathead minnows and *Ceriodaphnia* than ECF filtrates, but no acute lethal toxicity. Fathead minnows tend to be more sensitive to chlorine-containing effluents, while *Ceriodaphnia* are more sensitive to OZ filtrates.⁸⁷ By contrast, other studies of hardwood mill effluents indicate filtrates from a QZEopAEP sequence were slightly less toxic than those from a DEopDED sequence (using 16 and 25 m³ water/ton, respectively).⁸⁸ Cates et al.⁸⁹ recently showed Microtox toxicity decreased in the order: ECF softwood > ECF hardwood > TCF softwood > TCF softwood. A clearer understanding of how the toxicological properties of ozone filtrates compare to conventional filtrates depends on the identification and quantification of the primary toxicants in all types of filtrates.

Despite the complexity of the issue of toxicity of effluents, it is clear that fewer potential toxicants and other compounds will reach the aquatic environment when most of the bleach plant waste is recycled back to the recovery, and zero or near-zero effluent is discharged. Ozone bleaching is one way to achieve those goals. It remains to be determined whether emerging alternative approaches to mill closure, such as Champion's bleach plant filtrate recycle (BFR) of ECF filtrates,⁹⁰ will offset some of the current environmental advantages of ozone bleaching.

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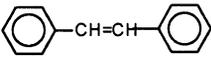
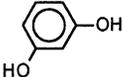
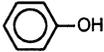
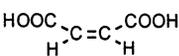
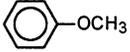
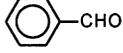
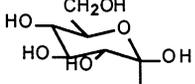
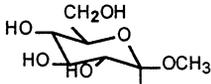
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TABLES

Table 1. Second-Order Rate Constants for Direct Reactions with Ozone.^a

Compound	Structure	pH	k $M^{-1} \cdot s^{-1}$	Scavengers
Styrene		3 in CCl ₄ ^b	3×10^5 1×10^5	t-Butanol -
Resorcinol		2	$> 3 \times 10^5$	Propanol
Phenol		1.7-2	1.3×10^3	Propanol
Maleic Acid		2 6	1×10^3 5×10^3	t-Butanol
Anisole			2.9×10^2	Propanol
Benzaldehyde		1.7	2.5	Propanol
Acetaldehyde		2	1.5	-
Glucose		2	0.5	-
Methyl β-Glucoside ^c		3	0.5	-
Glyoxilic Acid		1.5 - 5	0.2	t-Butanol
Formaldehyde		0.2	0.1	-

^a Values are taken from References 91 and 92 unless otherwise indicated.^b Reference 93^c Reference 5

FIGURE CAPTIONS

Figure 1. Potential Mechanisms of Hydrotrioxide Formation.

Figure 2. Ionic Mechanisms of Hydrotrioxide Decomposition.

Figure 3. Radical Mechanisms of Hydrotrioxide Degradation.

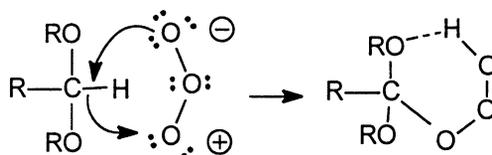
Figure 4. Ozone Cleavage of Glycosides.

Figure 5. Common Reactions of Ozone with Double Bonds (Rs refers to solvent).

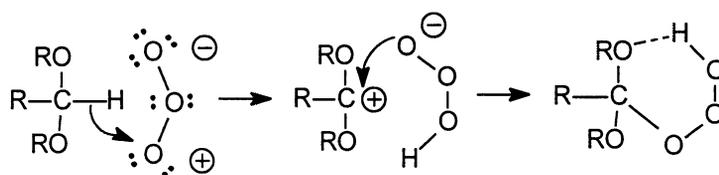
Figure 6. Reactions of Ozone with Aromatic Lignin Models.

FIGURES

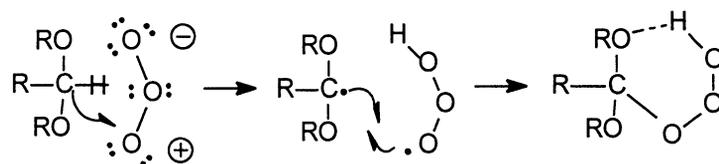
(a) 1,3 Dipolar Insertion



(b) Hydride Transfer



(c) Hydrogen Abstraction



(d) Oxygen Attack

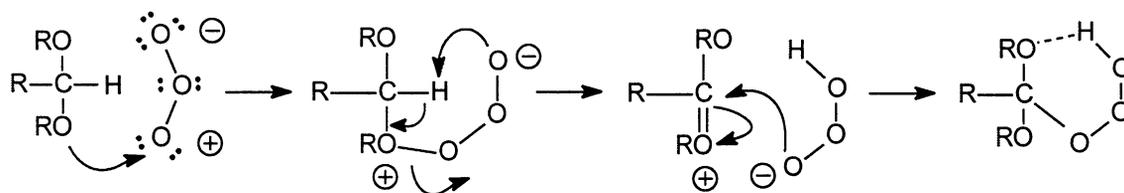


Figure 1. Potential Mechanisms of Hydrotrioxide Formation.

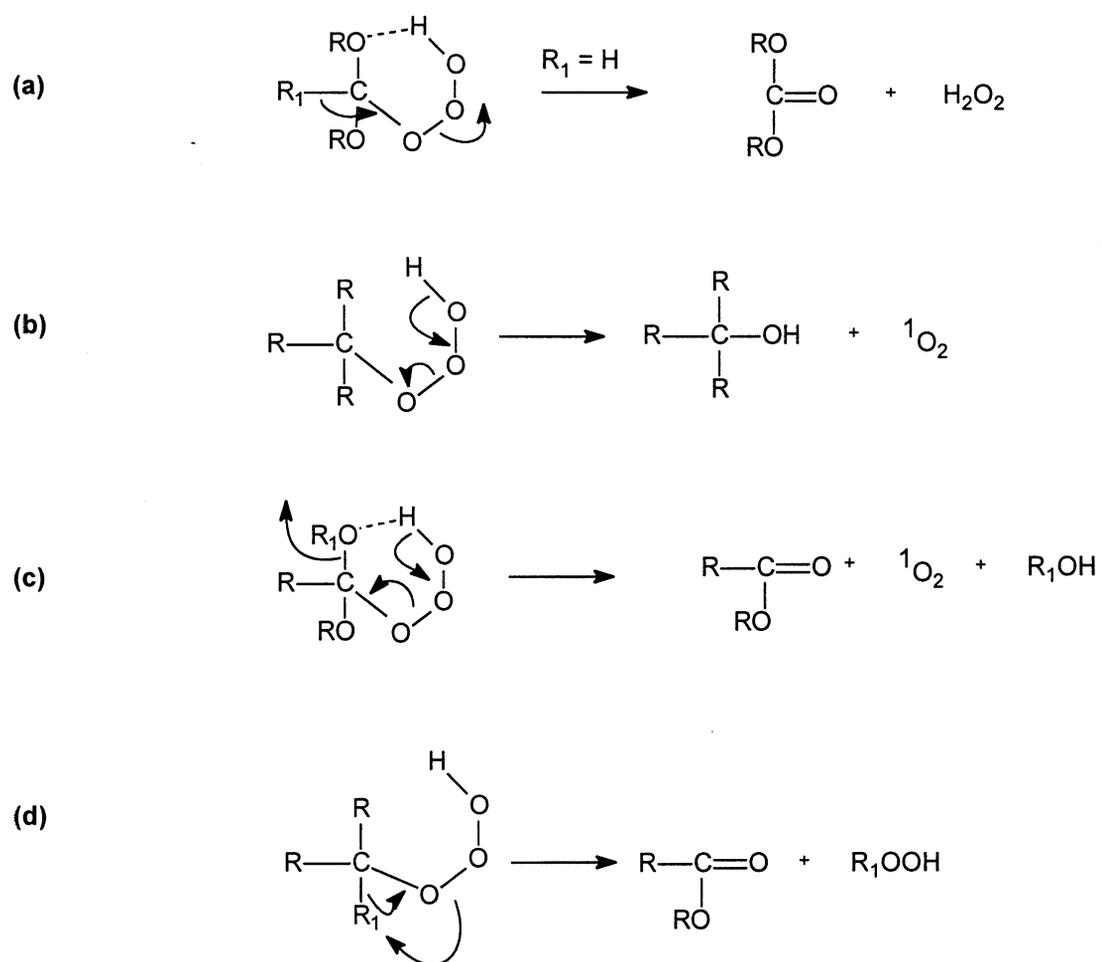


Figure 2. Ionic Mechanisms of Hydrotrioxide Decomposition.

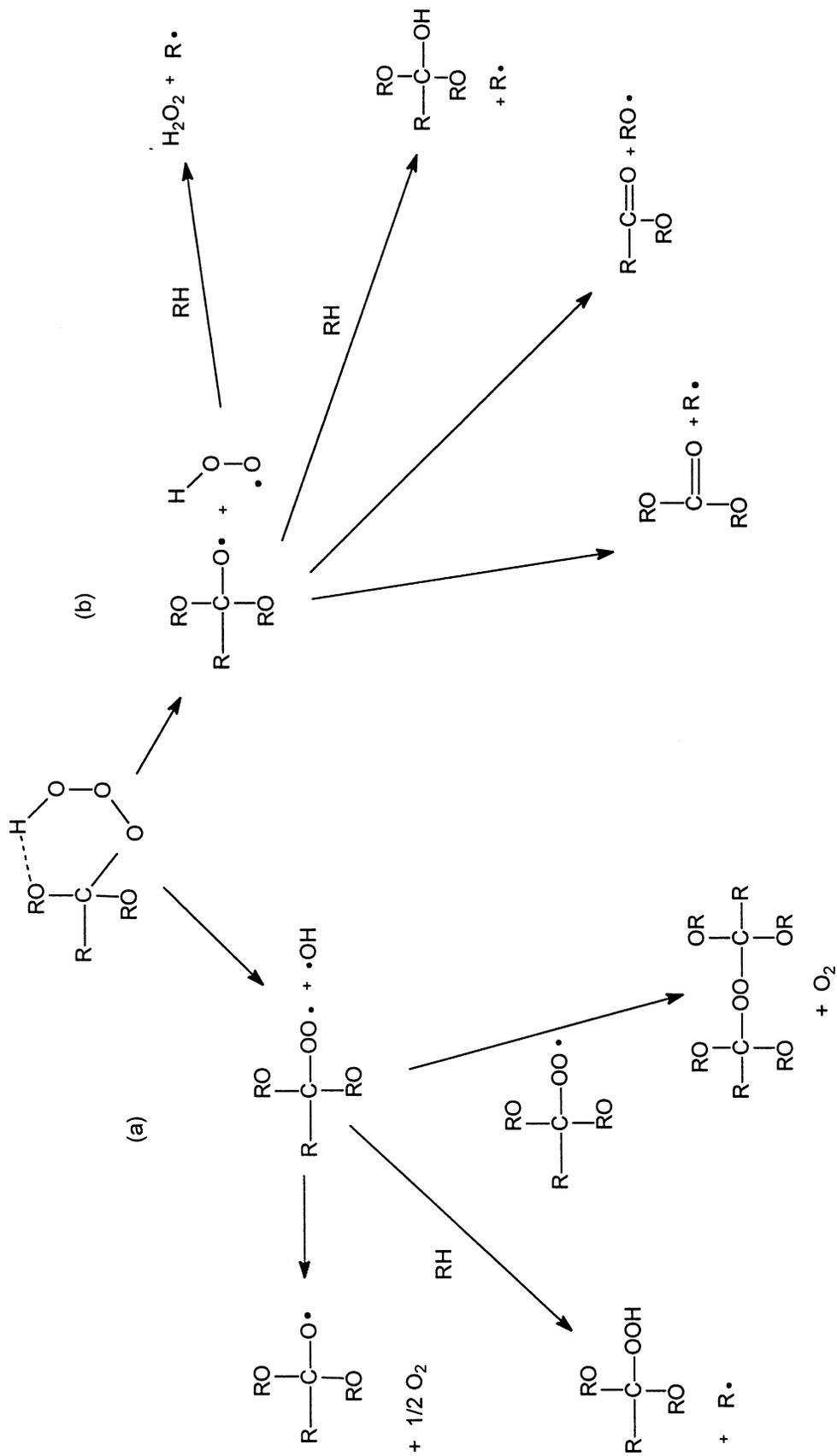


Figure 3. Radical Mechanisms of Hydroperoxide Degradation.

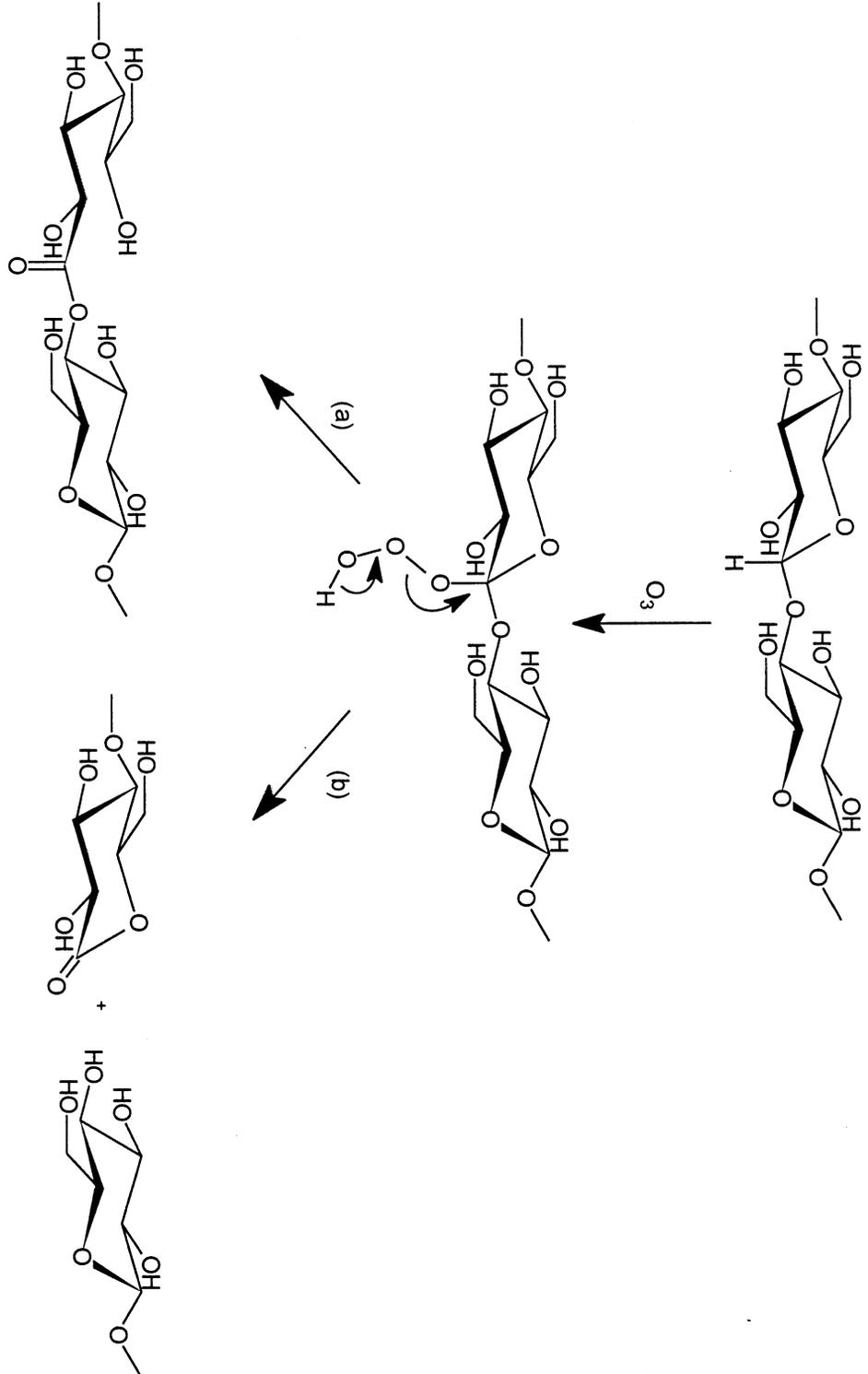


Figure 4. Ozonolysis of Glycosides.

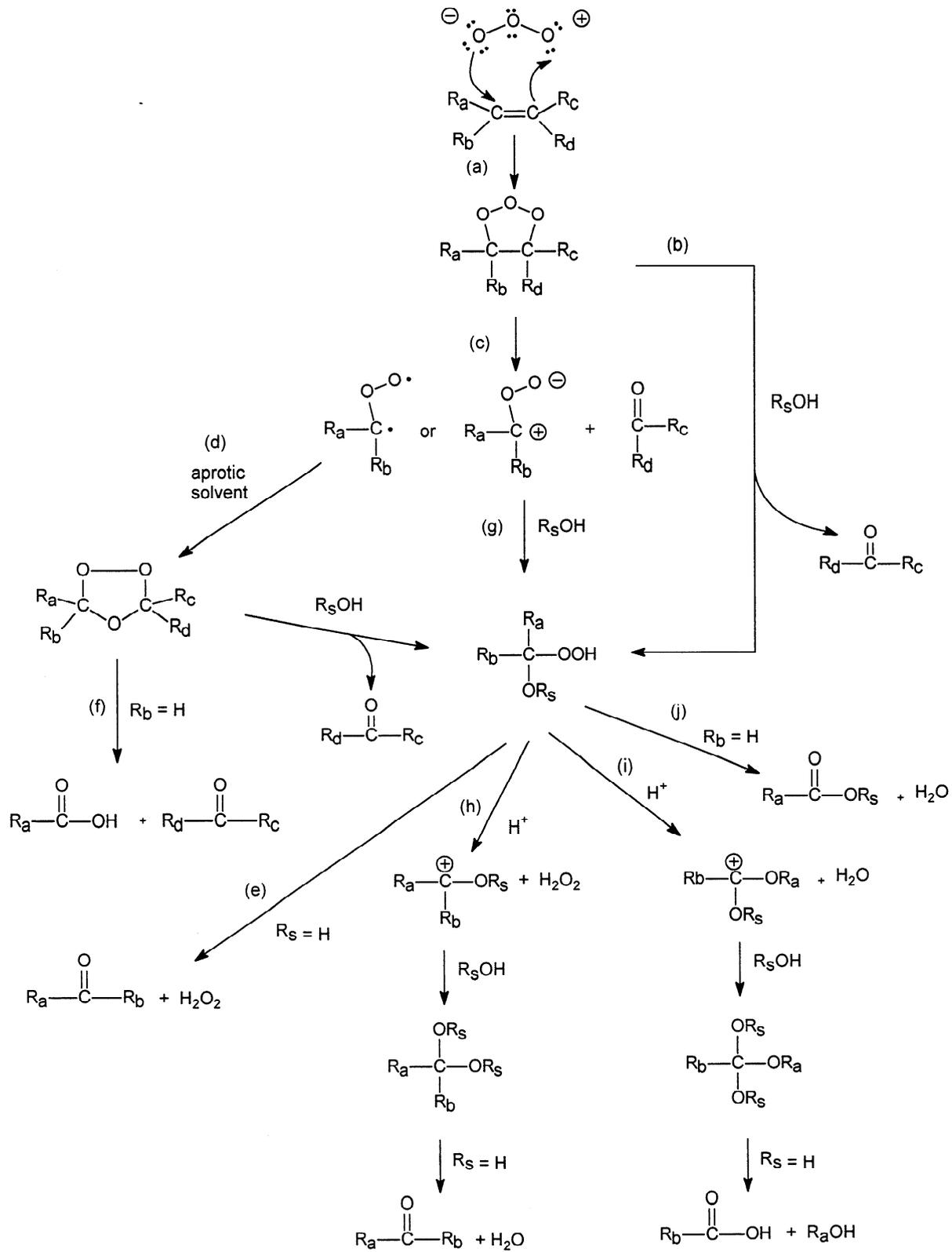


Figure 5. Common Reactions of Ozone with Double bonds (R_s refers to solvent).

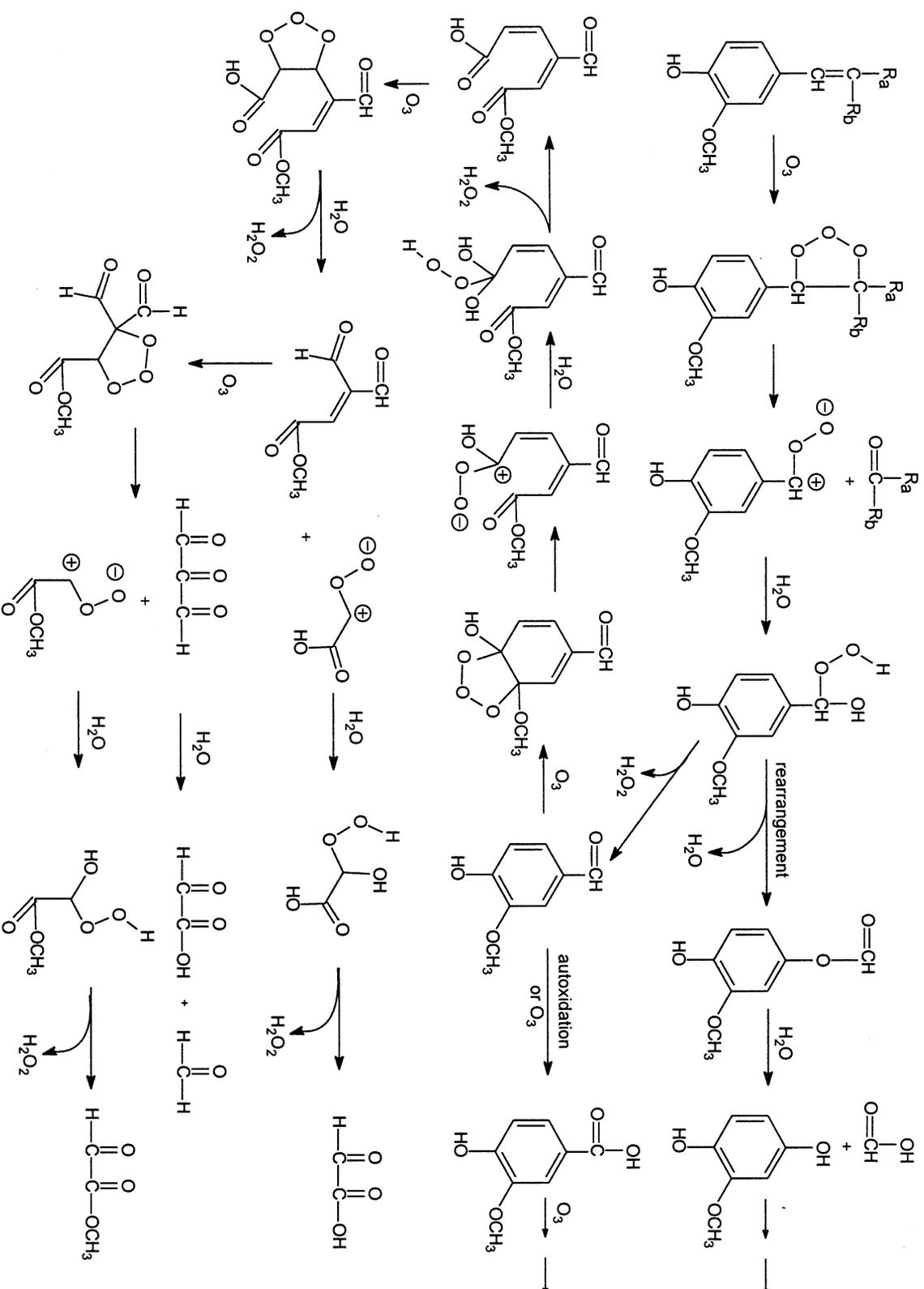


Figure 6. Reactions of Ozone with Aromatic Lignin Models.

