

**NONCHLORINE BLEACHING**

**Project 3388**

**Report One**

**PROGRAM FOR THE DEVELOPMENT OF AN  
OXYGEN-DERIVED BLEACHING TECHNOLOGY**

**A Progress Report**

**to**

**MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY**

**September 17, 1979**

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Despite many inconveniences and uncontrolled degradations, oxygen-derived bleaching chemicals represent the most likely basis for a technology to replace presently existing bleaching technology. A critical factor in the acceptance of this type of bleaching chemical is the undesirable degradation of carbohydrate materials by oxygen. This degradation arises from the action of powerful oxygen-containing intermediates on the pulp fiber. The mechanisms by which this degradation occurs are not known, but are thought to arise from a chain reaction initiated by very reactive, short-lived species such as hydroxyl radical and singlet oxygen. The longer lived superoxide radical anion is a poor oxidizing agent and an efficient radical scavenger.

An understanding of the action of the individual radicals (common to oxygen, ozone, peroxide and peroxy acid) on pulp will lead to the eventual understanding and minimization of carbohydrate degradation. The first steps of the program included a continual review of the literature and development of an experimental approach. These items are covered in this report.

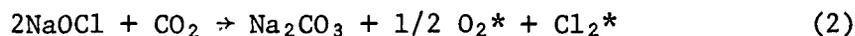
## INTRODUCTION

The environmental problems faced by the pulp and paper industry as a result of bleaching are being solved in different ways. The efficiency and technological convenience of the existing chlorine based technology has resulted in a desire to perpetuate that technology by using chlorine bleaching compounds in a more efficient manner (1). This is accomplished by changing bleaching conditions (such as using higher chlorination temperatures), by incorporating different amounts of chlorine dioxide into the chlorination stage (as suggested by Rapson) (2), by alternative high consistency-even gas phase reactions (3) (as typified by the Papribleach concept) (4), and by displacement bleaching techniques assisted by automated bleaching controls (5).

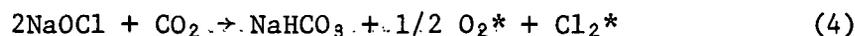
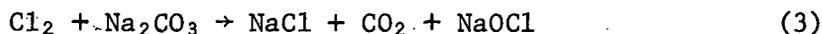
Suggestions have been made to use other novel chlorine-derived bleaching chemicals such as chlorine monoxide (6). This reagent is the anhydride of hypochlorous acid [Equation (1)] and is proposed to be used as a gas in conjunction with high consistency bleaching techniques. Little acceptance has been reported to date, however.



Other novel chlorine-derived bleaching chemicals which have been proposed are the so-called "nascent" gases [Equations (2) to (4)] (7). These have been tested as substitutes for chlorine and hypochlorite with limited success.

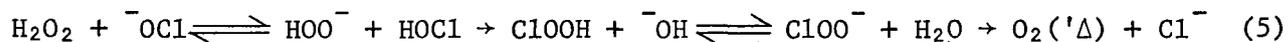


and/or



\*Claimed to be in "nascent" or atomic state (7).

The reaction between hypochlorite and peroxide has not been used as a source of bleaching chemical to date (8). This reaction is thought by some investigators [but not all (9)] to lead to singlet oxygen  $O_2('Δ)$  and/or  $O_2('Σ)$ .



Although these improvements and potential improvements can reduce the levels of chlorine compounds in bleach effluent to a great degree, they still do not eliminate chlorine from the bleach plant waste stream. The disposal technique designed by Rapson and his coworkers (10) is the most direct and practical approach yet considered for this purpose. His concept is based upon the experience of west coast pulp mills with salt impregnated logs which allows the sodium chloride to accumulate in the black liquor. Excess sodium chloride is eventually crystallized out of the liquors during the recovery process. It is postulated that the recovered sodium chloride could be used for chlorine regeneration.

The advantages of Rapson's process are that it uses existing equipment which need not be greatly modified. All organic chlorides are destroyed during combustion and no chlorine containing compounds will pass to effluent treatment equipment. The mill is not only isolated from the environment, but it decreases its dependence on external chemical supplies. This latter advantage is achieved only by expenditure of energy which might be greater than that required by a chemical manufacturer.

The disadvantages of the process are that additional space and equipment be available. Corrosion of recovery units by chloride ion is likely if they are not made of resistant materials. Foam has been a problem at the Great Lakes Forest Products, Ltd. mill in Thunder Bay, but this problem will probably be eliminated (11). The problem of what to do with excess sodium chloride has not been solved.

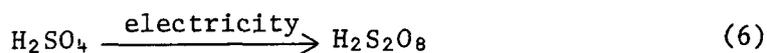
Some of the excess might be used to regenerate chlorine, but it is unlikely a mill could compete with commercial sources for the production of sodium chlorate necessary for chlorine dioxide manufacture.

Other modifications of Rapson's concept can be imagined in which the waste bleach liquors are not recycled to the recovery furnace but are treated directly. Duplication of recovery units is impractical; some thought might be given to the possible use of wet combustion techniques combined with the use of catalytic beds to increase their efficiency (as was reported during an early phase of Project 3265). The system was suggested for Project 2500 and requires balances in the sodium and chlorine contents of the incoming liquor. Ultimate disposal of waste salt still has not been solved.

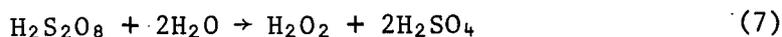
### ALTERNATIVE BLEACHING

Numerous alternative chemicals to chlorine-derived reagents can be used to bleach pulp. Few have the potential of rendering an efficient technology obsolete since few elements combine a range of valence states capable of oxidizing and reducing organic substances, together with effective processes, to minimize effluent problems. Chemicals such as permanganates (12), dichromates (13), and uranium salts (14), can bleach pulps but present more difficult preparation and disposal problems than the chlorine derived technology.

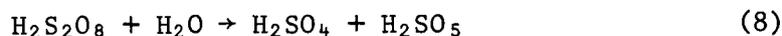
Sulfur chemicals offer a better possibility since they make available a wide range of oxidizing and reducing agents combined with an existing technology for sulfur recovery. Some of these reagents such as sulfur dioxide, sulfurous acid, and dithionite ions are already used in the pulp and paper industry. The electrolysis of sulfuric acid to persulfuric acid offers the possibility of using several other unique oxidizing agents (15). This reaction was formerly used for the



the production of hydrogen peroxide before being displaced by the autoxidative processes now in use (15). Although persulfuric acid has many properties similar to peroxyacetic acid, the necessity to use it in strongly acidic solutions makes its use in the paper industry unlikely. Instead, it can be converted to hydrogen peroxide as follows:



Caro's acid ( $\text{H}_2\text{SO}_5$ ), a powerful oxidant as yet untested in bleaching, can also be derived from persulfuric acid and is sometimes thought to be an intermediate in the formation of hydrogen peroxide. It too must be employed in acidic media.



Hydrogen peroxide can be generated and used as a bleach. If the cost is low enough, peroxyacetic acid and other organic peroxides can be synthesized from it or directly from persulfuric acid to provide more specific bleaching actions.

By dealing only with sulfur technology, a wide range of useful chemicals become potentially available such as the following:

$S^=$ ,  $SO_2$ ,  $SO_3^=$ ,  $SO_4^=$ ,  $S_2O_4^=$ ,  $S_2O_8^=$ ,  $SO_5^-$ ,  $O_2^=$ , peroxy acids, organic peroxides

In theory, the sulfur compounds could be recycled into kraftlike recovery furnaces if the organic load were great enough. However, several serious disadvantages do exist. Present kraft recovery units could be overloaded and expanded (expensive) facilities could be required. The key chemical — persulfuric acid — is energy intensive. There is no guarantee that this untried system of oxidizing and reducing agents could actually bleach pulp effectively. In all likelihood, sulfur emission problems would be intensified, detracting from efforts to make a mill environmentally acceptable.

Thus, by a process of elimination, the use of oxygen as a source of bleaching chemicals appears a better alternative to the use of sulfur compounds. Like sulfur technology, oxygen technology can lead to the formation of a wide range of chemicals of differing oxidation characteristics. However, as no additional sulfur is introduced, recovery difficulties should not be increased. Also, many of the chemicals potentially available from an oxygen based bleaching technology have been tested and proven to be effective (though possibly expensive) bleaching chemicals.

The use of oxygen for bleaching is not new. In antiquity it was used in conjunction with light. More recently manganese salts were employed to overcome uncertain induction periods (13). Degradation was probably not excessive because elevated temperatures were not employed. The process was very inefficient compared

to even the simplest chemical process developed during the industrial revolution, and for that reason did not gain prolonged acceptance.

The extensive use of oxygen in modern times is hindered by excessive degradation of the carbohydrate component of the pulps. This degradation has been minimized by several developments. Magnesium ion is sometimes effective in decreasing pulp degradation if contaminating metal ions are present (16). This discovery probably provided some of the incentive for a more careful examination of the pulping and bleaching potential of oxygen. Control of reaction parameters such as pH, chemical to wood ratios, chemical charge, consistency, time and temperature coupled with the development of satisfactory equipment which would ensure oxygen penetration has done much to minimize pulp degradation and encourage industrial acceptance (17).

High consistency processes such as those represented by the Sapoxyl and MoDo-CIL processes were initially employed to increase oxygen availability to the pulp fiber. Better control of pH, oxygen concentration, and reaction temperature is thought to result when low consistency processes (such as those of HOPES, Airco and International Paper Company) are employed (18). The advantages of the high and low consistency processes are claimed to be optimized by medium consistency processes being developed by Kamyr and Black Clawson-Kennedy.

Conventional and patent literature is flooded with other esoteric means to optimize oxygen delignification processes. These may be classified as those that attempt to modify the lignin in some manner before reaction occurs and those that influence the progress of the oxidation during bleaching. Examples of the former concept are the use of sulfur-containing additives patented by International Paper Company (19), multistage pretreatments before oxygen delignification [by ESPRA

(20)], peroxyacetic acid pretreatments attempted in IPC Project 3289 and use of  $\text{ClO}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{NaBH}_4$  pretreatments described in IPC Project 3092. The use of additives to control the bleach is much more common than pretreatment. They range from the addition of magnesium ions (in the form of various salts and complexes) to organic substances such as alditols, amines (21), formaldehyde (21), potassium iodide (22), and various complexing agents with and without the presence of added transition metal ions (23). Numerous other conceptions abound in the patent literature (24) but it is unlikely that many of them have received commercial acceptance.

A chlorine-free bleaching system will require more stages than a single oxygen delignification. Other bleaching chemicals and stages must be employed to provide the required product. These supplemental chemicals can be derived from oxygen. Peroxides, peroxyacetic acid, and ozone have unique bleaching characteristics that supplement the bleaching action of oxygen. Bleaching experience suggests the incorporation of these oxygen-derived bleaching chemicals must be done with some care, since oxygen-derived chemicals are prone to degrade pulp. This undesirable feature of oxygen-derived bleaching chemicals will probably be increased in bleaching systems based entirely on oxygen and its derivatives.

Current literature suggests that oxygen-peroxide bleaching sequences are of limited value (25) although oxygen-ozone sequences are thought to be more effective. Final bleaches with organic peroxides would probably parallel the effect of hydrogen peroxide whereas the effect of peroxy acids would probably resemble that of chlorine dioxide.

### MECHANISMS OF OXYGEN DEGRADATION OF PULP

Early investigators quickly saw a parallel between the cellulose degradations that occur during oxygen bleaching and those that occur during the alkali aging of cellulose employed during viscose manufacture [see summary in Ref. (16)]. Hydrogen peroxide was detected in some reactions and parallels were drawn on the effect of transition metal ions in the two systems. Although the exact mechanism of the degradation during viscose aging and oxygen delignification is uncertain, the reaction of pulp with oxygen exhibits many of the characteristics of classical autoxidation reactions (26). Besides the presence of peroxides, the consumption of oxygen (and pulp degradation) exhibits induction periods, rapid rates of reaction and degradation after initiation, as well as susceptibility to catalysis and auto-inhibition (and, hence, changing reaction kinetics) with reaction time (27). This behavior is a reflection of the classical kinetic autoxidation pattern of initiation, propagation, and termination stages during reaction.

Modern research indicates that some of the active participants in this autoxidative degradation are the various reduced states of oxygen as well as organic radicals of various types derived from wood components. These include singlet oxygen, hydroxyl radicals, peroxides, and the various conjectured forms of the perhydroxyl radical. These intermediates are derived from all oxygen-based oxidants such as oxygen itself, peroxides, dioxetans, peroxy acids and ozone, and complicates their otherwise specific delignification action. This specific oxidative action can frequently be accomplished in the laboratory but seldom under mill conditions.

The reaction of oxygen itself with organic substances occurs because oxygen is a diradical. The reaction is initiated as a result of the reaction of the organic substrate with heat or light to form a radical, or with alkali to form electron-rich centers which can combine with oxygen. The products of this

reaction are the oxygen-derived intermediates described previously and organic radicals. The complexity of this interaction is still subject to considerable debate. It is thought by Singh (28) that the reaction characteristics of a radical species (dependent upon outer electrons) can alter during autoxidative reactions. He does not state whether these changes are the result of chemical actions or are spontaneous transformations. The relationships for superoxide radical, a, hydroxyl radical, b, and ozone, c, illustrated by him are shown in Fig. 1.

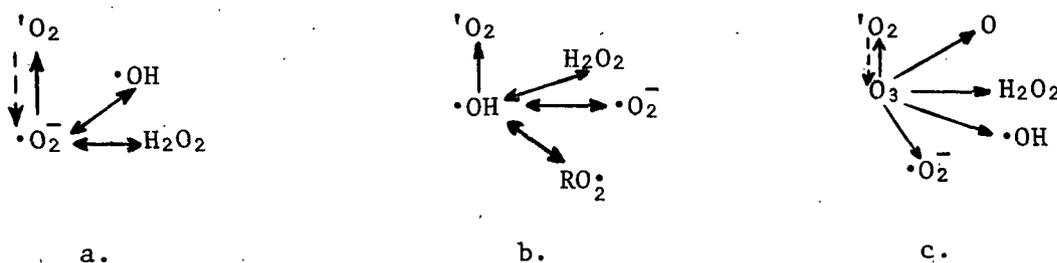
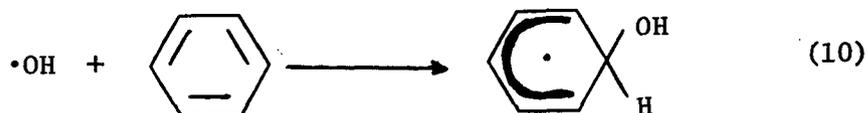
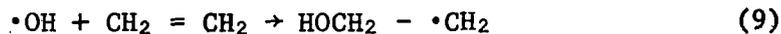
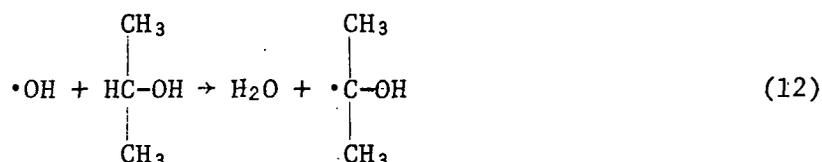
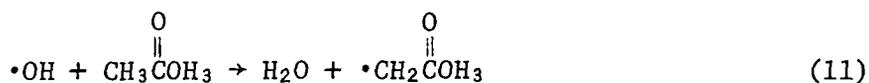


Figure 1. The Relationships Between Oxygen Radicals Suggested by Singh (28)

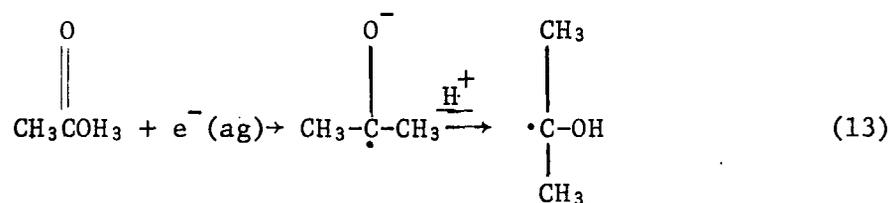
Although it is difficult to maintain only one radical species during autoxidation, pulse radiolysis experiments have partially achieved this goal and made some of the chemistry of the radicals known (29). The most powerful oxidant-hydroxyl radical and oxyanion ( $\cdot\text{OH}$  and  $\cdot\text{O}^-$ ) readily attack organic molecules as well as positively and negatively charged ions. Its short half-life complicates its study but it has been shown to add readily to unsaturated and aromatic substances [Equations (9) and (10)].



Hydrogen abstraction is the novel reaction with saturated organic compounds, including those containing carbonyl groups. Weaker C-H bonds are broken in preference to stronger bonds. Inductive effects influence the site and rate of radical attack since it is a strongly electrophilic reagent.



The ketyl radicals produced by the attack of  $\cdot\text{OH}$  on the hydrogen atoms of alcohols can also be formed by the action of hydrated electrons on carbonyl compounds: [compare with reaction (11)].



In the case of polyhydric alcohols, the ketyl radicals decompose by elimination of water to give less strongly reducing radicals:



The oxygen radical ion ( $\cdot\text{O}^-$ ) does not add as well to aromatic compounds as  $\cdot\text{OH}$ , it is less effective in oxidizing inorganic ions and reacts with oxygen to form the ozonide ion ( $\cdot\text{O}_3^-$ ). Recent research by Lindgren and Sundin (30) has demonstrated the action of hydroxyl radicals on carbohydrate models is not affected

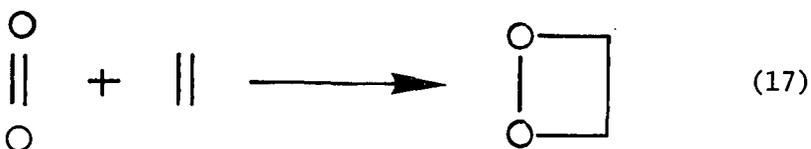
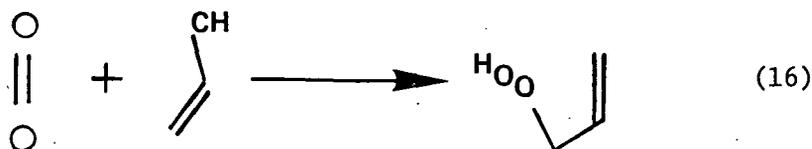
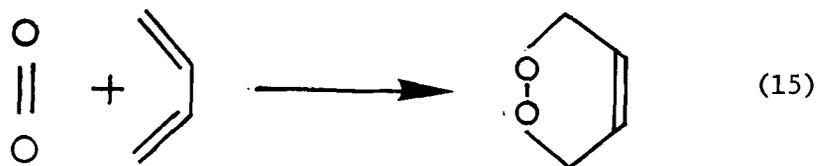
by transition metal ions and they propose cellulose degradation results in part from the formation of these radicals by the action of metal ions on other intermediates.

Singlet oxygen has been proposed to be a reactive intermediate in the reactions of pulp in the presence of oxygen, but proof of this conjecture is not available. Some physical properties of these unusual energy states of oxygen and their approximate valence representations are given in Fig. 2 (31).

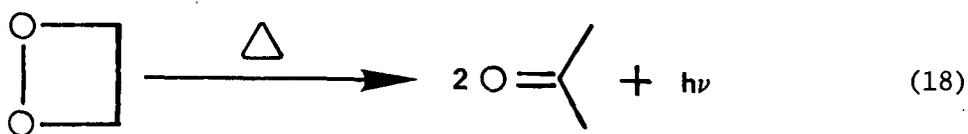
Electronic States	Highest Occupied MO's	Relative Energy (kcal)	Lifetime (sec)		Valence Bond Structures
			Gas Phase	Liquid Phase	
$^1\Sigma$		37	7-12	$10^{-9}$	
$^1\Delta$		22	3.000	$10^{-3}$	
$^3\Sigma$		0	$\infty$	$\infty$	

Figure 2. Lowest Electronic States of Molecular Oxygen and Their Properties

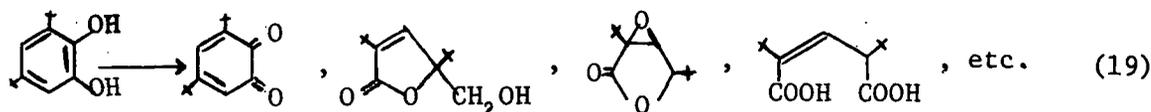
The more reactive form of singlet oxygen degrades very rapidly to a less reactive form whose chemistry is being investigated. The former state behaves in a radical-like manner, whereas the less reactive form is isoelectronic with ethylene and reacts as a dienophile because of its electrophilic nature. The peroxides formed as a result of 1-4, 1-3 and 1-2 additions [shown in Equations (15), (16), and (17)] provide a new source of radicals.



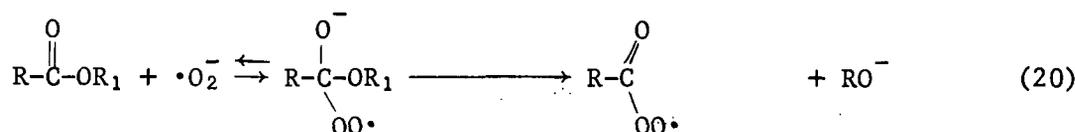
Most common is the 1-4 addition to various organic molecules, Giertz has suggested the formation of dioxetans as a result of the reaction of lignin with oxygen (32) although endoperoxides (analogous to 1-4 addition products) might also explain his data. Although some dioxetans have been isolated, they are highly unstable and decompose explosively at room temperature with the emission of light. If these many conjectures are true, even the photoexcitation of organic molecules during oxygen delignification is also conjecturable.



The potential utility of the superoxide radical and the corresponding radical anion ( $\cdot\text{O}_2^-$ ) is very great. Research has shown this radical is not a powerful indiscriminant oxidant. The superoxide ion can oxidize orthophenolic groups such as those present in 9,10-dihydroxyphenanthrene and 3,5-di-tert-butyl catechol, to a variety of products (34,35).

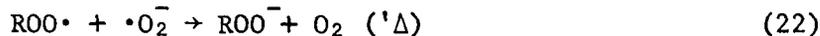
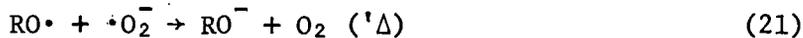


Esters are hydrolyzed via an initial reversible addition of  $\cdot\text{O}_2^-$  to the carbonyl carbon followed by loss of alkoxide from the tetrahedral intermediate. Aldehydes and ketones undergo initial addition of  $\cdot\text{O}_2^-$  but they lack a viable leaving group which precludes a net reaction (36,37). Decomposition products from  $\cdot\text{O}_2^-$

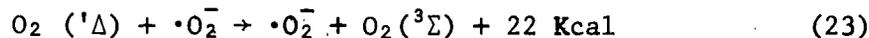


(probably  $\cdot\text{O}_2\text{H}$ ) are highly reactive and lead to Cannizzaro-type reactions.

Superoxide radical is closely associated with the existence of singlet oxygen. The latter is formed as a result of the reaction of superoxide and organic peroxy-radicals (38):



Superoxide quenches singlet oxygen (39) — a finding which mitigates against the production of singlet oxygen by the dismutation of superoxide mentioned earlier.



Russian research has led to the conclusion that  $\cdot\text{O}_2^-$  complexes with transition metal ions [see references in (40)]. It was postulated that coordinated  $\cdot\text{O}_2^-$  may act either as a strong oxidant resembling the hydroxyl radical ( $\cdot\text{OH}$ ) or as a powerful terminal electron acceptor in complex multistage oxidation processes.

This sensitivity of superoxide radicals to catalytic influences is in marked contrast to the insensitive nature of the more powerful hydroxyl radical to catalysis. Superoxide radical is, therefore, a reactive and highly controversial radical component present during oxygen delignification.

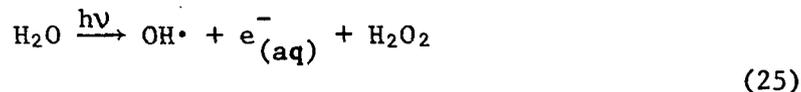
GENERATION OF RADICALS BY MEANS OF RADIATION CHEMISTRY

Water is an ideal source of radicals common to oxygen delignification reactions. Generation is achieved using radioactive sources and electron discharges from a van der Graaf generator. Many fragments are produced by these bombardments. Most species are hydrated within about  $10^{-9}$  seconds although controversy exists about the extent of hydration of free electrons. The yield of fragments must account for the number of water molecules lost. The radical and molecular yields  $10^{-8}$  seconds after irradiation by the passage of a charged particle are related by:

$$G_{-H_2O} = 2H_2 + G_H + G_{e(aq)} = 2G_{H_2O} + G_{-OH} \quad (24)$$

where a G unit is equivalent to one molecule of the specified fragment formed or destroyed for every 100 eV of energy absorbed. Each of the reactive species can react with water or other reactive species until limiting concentrations are achieved. The reactions are, therefore, of no use in preparing concentrated peroxidic solutions. Thus, the irradiation of water within wide ranges (0.1-20 MeV) yields a complex mixture of products whose equilibrium concentrations at different pH are shown in Fig. 3 (29).

It is possible to control this complex mixture of radicals by means of water soluble additives. For example, Lindgren and Sundin (30) studied the reactions initiated by irradiating an aqueous alkaline solution of glycerol and extrapolated their results to speculate on the effects of oxygenated radicals on cellulose. Their system used a Co radiation source to produce the following radicals initially:



where G = 2.8      3.1      0.6

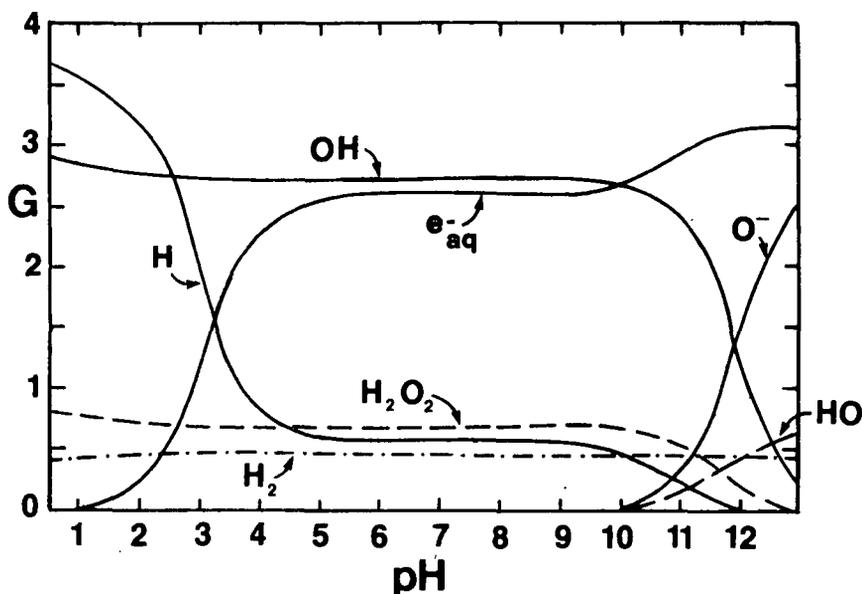
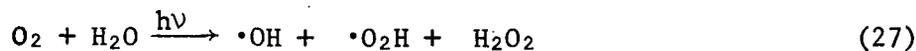


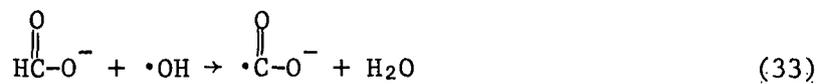
Figure 3. Effect of pH on the Primary Products of Water Irradiation. Yields are for  $\gamma$ -rays and Fast Electrons with Energies of the Order of 0.1 to 20 MeV and Assume that OH and  $H_2O_2$  Achieve Acid-base Equilibrium. The Yields of H and  $e_{aq}^-$  are the Amounts of These Species Which Would React with  $10^{-3}M$  Scavenger(s) if  $k(e_{aq}^- + S) = 2 \times 10^{10}M^{-1} \text{ sec}^{-1}$  and  $k(H + S) = 10^7M^{-1} \text{ sec}^{-1}$ .

The hydrated electron can react further to destroy the effectiveness of this radiation [Equation (26)]. Fortunately, the behavior of this free electron and the concentration and type of radical species can be controlled by additives. The presence of oxygen in the irradiated solution leads to the production of perhydroxyl radicals and a mixture of radicals is the final result.



where G           •    2.8    3.1    0.6





Ethylenediamine tetraacetic acid (EDTA) could be added to minimize trace metal catalysis, since a 100-fold excess of formate protects EDTA from attack by hydroxyl radicals. The concentration of perhydroxyl radical was determined by reaction with ferricytochrome C and nitroblue tetrazolium.

## GENERATION OF RADICALS BY CHEMICAL MEANS

Other alternatives for the generation of radicals are also available in addition to those mentioned previously. Superoxide radical can be prepared by several techniques. It can be generated in pyridine solution by electrochemical reduction of  $O_2$  at a gold electrode. The concentration of superoxide (about 5  $\mu M$ ) was monitored by linear sweep voltammetry (41).

Potassium superoxide ( $KO_2$ ) provides yet another source of radicals. The reactivity of  $KO_2$  was not extensively studied until recently because of its instability in water and its insolubility in organic solvents. It has recently been demonstrated that 18-crown-6-ether promotes the solubility of  $KO_2$  in organic solvents by complexing with potassium ions (41). It is equally possible the crown ether will assist the dissolution of  $KOH$  in organic solvents. Known solvents include DMSO, methylnitrite, benzene and pyridine.

Ozone decomposition is catalyzed by hydroxyl ions as well as by radicals which can serve as carriers of a chain reaction. Decomposition of  $O_3$  to radicals frequently competes with the direct consumption of  $O_3$  by solutes. According to Hoigne and Bader (40) hydroxyl radicals are the main oxidants formed when ozone is decomposed at high pH levels. The possibility exists that useful mixtures of radicals may be generated when solutions of ozone are mixed with caustic solutions. It is also possible that the proportions of the radical species can be controlled by the addition of  $O_2$ ,  $N_2O$  or sodium formate as was done in the case of irradiation experiments.

#### PROPOSED INVESTIGATION

The initial experiments will involve the study of the reaction of pulp fibers and selected model substances with the superoxide radical anion dissolved in a suitable organic solvent (probably pyridine). This approach will permit the development of analytical techniques and the evaluation of the effect of superoxide radical anion during lignin removal. A comparison with pulp behavior during oxygen bleaching will show whether this radical species might contribute to the reaction but does not prove whether it actually does so.

This experimental system will also permit an initial evaluation of the effect additives and other catalytic influences have upon the conjectured participation of the superoxide radical anion during delignification.

The reaction of radicals with pulp in an aqueous system is a more meaningful study from the point of view of the paper industry. Consideration will be given to the generation of aqueous solutions of radicals. The short half-life of the hydroxyl and superoxide radicals, as well as that of singlet oxygen makes it difficult to apply the classical radiation techniques of generation to the study of pulp slurries. Instead, it is hoped chemical methods of generation employing ozone, peroxides, or electrolytic processes can be developed.

The decomposition of ozone in NaOH is claimed to result in the generation of hydroxyl radicals. If the extent and selectivity of the reaction were known, the technique could provide a source of radicals in aqueous solution. The approach would have the additional value of extending our knowledge of ozone chemistry. The decomposition of peroxide to hydroxyl radicals can be induced photochemically. Since peroxide reacts very slowly with pulp at 5-10°C, any pulp degradation in peroxide solutions at that temperature could reflect the influence of suitable radiation. Electrolytic methods of radical generation have been reported in the literature

in both aqueous and nonaqueous systems. These techniques also deserve consideration as an alternative procedure for the preparation of aqueous solutions of selected radicals.

The effects of singlet oxygen and atomic oxygen during delignification must also be considered. Methods of generation and reaction with pulp are still under consideration.

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