

THE CHEMISTRY OF DELIGNIFICATION IN PULP BLEACHING

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INTRODUCTION

The commercial bleaching of pulps represents a chemical process by which the residual non-carbohydrate constituents, principally lignin, are removed from the pulp. The colour improvement in the process is due to the fact that the chromophoric groups responsible for the discoloration are chemically combined with the latter constituents and are effectively removed from the pulp when these are dissolved in the bleach liquor.

Obviously, an effective delignifying bleaching chemical has to fulfil two essential conditions as far as its chemical characteristics are concerned. Firstly, it must react rapidly with lignin, degrading it to water and/or alkali-soluble fragments, and, secondly, its action on carbohydrates, particularly cellulose, must be extremely slow compared with the rate of reaction with lignin.

The same requirements are valid for reagents which are used for the preparation of holocellulose and various other cellulose preparations from extracted wood meal. It is interesting to note that for each commercial bleaching procedure, there exists a method for the preparation of holocellulose, or various other "cellulose" preparations, that utilizes the same agent and a largely similar set of conditions. This parallelism,

Table 1. Bleaching methods compared with holocellulose preparation methods

<i>Reactant</i>	<i>Pulp bleaching method</i>	<i>Counterpart holocellulose method</i>	<i>Ref.</i>
Molecular Cl_2	Acid chlorination	Cl_2 -ethanolamine-holocellulose	2
HOCl	Hypochlorite bleaching	Norman-Jenkins-cellulose	3
ClO_2	ClO_2 bleaching	Schmidt-holocellulose	4
NaClO_2	Chlorite bleaching	Wise-holocellulose	5
Peracetic acid		Poljak-holocellulose	6
Nitric acid		Kürschner-Hoffer-cellulose	7

illustrated in *Table 1*, is by no means obvious, if one takes into account that the residual lignin in pulps differs from wood lignin by the pulping and, sometimes, by the pre-bleaching operations.

Some of the delignifying agents listed, however, have not found application as industrial bleaching agents. Nitric acid, although an excellent delignifying agent, reacts too quickly with cellulose to be utilized for pulp

bleaching. The new bleaching agent peracetic acid shows considerable promise as a bleaching chemical and is at present being studied in a number of laboratories.

In the bleaching process, the pulp constituents cellulose, hemicelluloses and lignin all compete for the consumption of the bleaching agent. A situation where the rate of the lignin reaction is very high in comparison with the rate of cellulose degradation is most advantageous for a successful operation. A convenient method for studying this ratio of reactivities was developed by Paulson¹ and consists of plotting the fluidity of the pulp against the consumption of the bleaching agent. The method forms an excellent basis for comparison between different bleaching agents and conditions, and is limited only by the fact that the action of the bleaching agent does not consist of one but several parallel and consecutive reactions.

A more thorough understanding of bleaching phenomena would involve the chemical pathways by which lignin is degraded to soluble compounds. Work in this area presents several difficulties which cannot easily be solved by studying actual bleaching systems. Some of these difficulties can be avoided by studying the reactions of wood lignin itself, or those of various lignin preparations, with bleaching agents. Furthermore, studies on lignin model compounds are of considerable help in evaluating these complex reactions.

One of the outstanding questions in bleaching chemistry is concerned with the site of the primary attack by the reactant. The agent, depending on its chemical nature, may attack the guaiacyl propane units either at the aromatic nuclei or, alternatively, it may react with the three carbon side chain of these units. *A priori*, the former possibility would seem to be the more likely one, particularly if the bleaching reagent has strongly electrophilic characteristics, because the reactivity of the aromatic nucleus is enhanced by the phenolic hydroxyl, phenol ether and side-chain substituents.

In testing the reactivity of the aromatic nuclei and that of side-chain α -carbon atoms in lignin, simple model compounds, such as vanillyl and veratryl alcohols and their derivatives, are particularly useful. It is well known that model studies on the compounds mentioned have made an important contribution to the understanding of pulping reactions. The problem of elucidating the reactivity of β - and γ -carbon atoms is a more difficult one and no well-defined approach for solving the problem is available at present.

In the following, a brief review is presented on the current ideas of the mechanism of degradation of lignin by various bleaching agents.

CHLORINE-WATER SYSTEMS: CHLORINATION AND HYPOCHLORITE BLEACHING

In aqueous chlorine systems, chlorine can exist in three different forms, depending on the pH of the solution. These are molecular chlorine (Cl_2), hypochlorous acid (HOCl) and its anion OCl^- . In the region up to pH 5, a concentration-dependent equilibrium exists between molecular chlorine and hypochlorous acid, while at higher pH values hypochlorous

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acid and its anion are both present in proportions directly determined by the pH of the solution.

Two pH regions are of particular interest for bleaching chemistry. The pre-chlorination of pulp is carried out at pH 2, and the purpose of this operation is to make the bulk of the residual lignin soluble in both water and alkali. No colour improvement of pulp is accomplished at this stage, nor in the following alkali-wash, but the subsequent hypochlorite bleaching stage is greatly facilitated because of the decreased residual lignin content. The optimum region for the hypochlorite bleaching is pH 8-9, and the effect of the bleaching at this pH differs significantly from that of pre-chlorination.

The difference between the effects of pre-chlorination and hypochlorite bleaching is probably due to the difference in the nature of the reacting chlorine species. At the lower pH, molecular chlorine, a species much more reactive than hypochlorous acid, directs the reaction, while in the hypochlorite bleaching, hypochlorous acid, or a reactive intermediate derived from it, probably plays the rôle of the primary attacking species.

The effect of molecular chlorine on lignin and lignin models has been subject to more extensive studies than the hypochlorite oxidation. Several

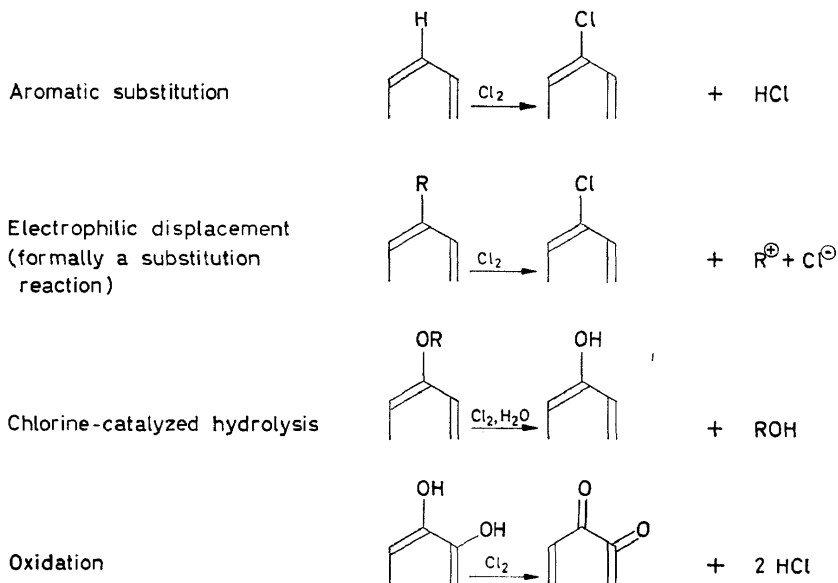


Figure 1. Competing reactions in the chlorination of aromatic compounds

reactions take place which can be classified in four classes illustrated in Figure 1. The reactions are shown in the approximate sequence of decreasing reaction rates, although it should be borne in mind that considerable variation in rate exists in each class of reactions.

(a) Chlorine substitution

The rate of this reaction is immeasurably fast in the guaiacyl propane units and takes place at the 6- and 5-positions of the aromatic nucleus. The rate constants at these positions depend on the presence or absence of a free phenolic hydroxyl group at the 4-position as well as on the nature of the aliphatic side chain at position 1. This reaction does not contribute to the degradation of lignin.

(b) Side-chain displacement

This reaction is formally analogous to the substitution reaction, except that the leaving group is a carbonium ion instead of a proton. In etherified

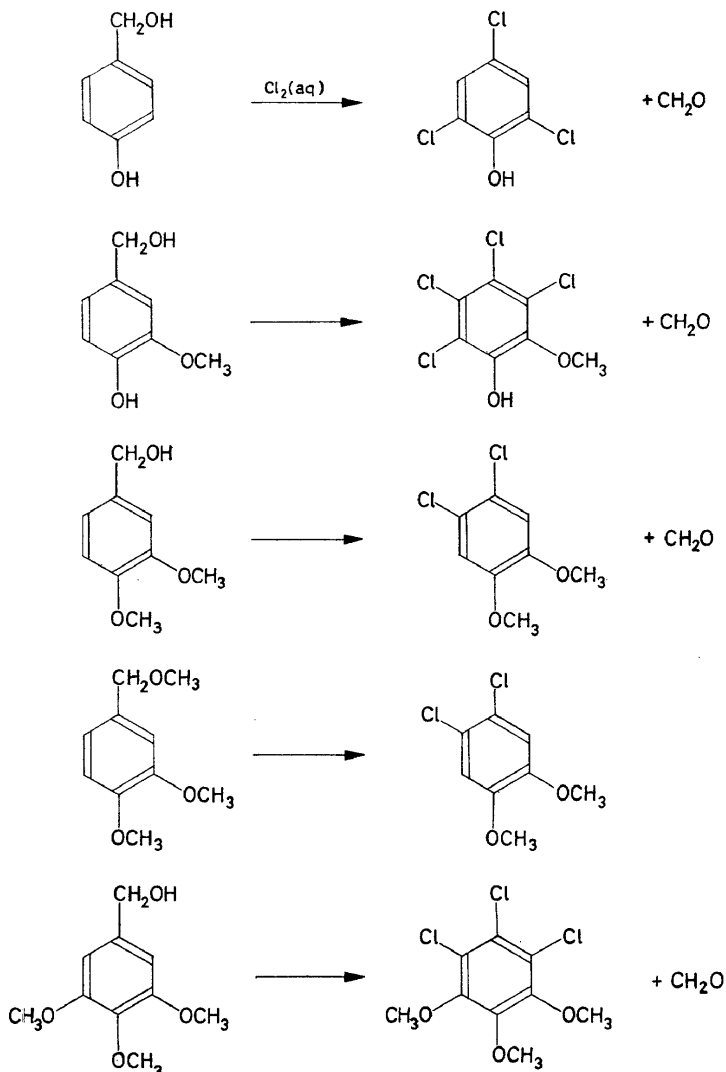


Figure 2. Reactions of primary *p*-hydroxybenzyl alcohols and their ethers with chlorine

units, at least α -carbinol and α -ether groups can be displaced easily. The rate of the reaction appears to be of the order 1/10 of the rate of corresponding substitution reaction in the case of a primary carbinol group⁸.

A free phenolic hydroxyl group in position *para* to the side-chain exerts an enhancing effect on the displacement reaction. In addition to carbinol and carbinol ether groups, also α -carbonyl and carboxyl groups can be displaced rapidly.

(c) The hydrolysis of aromatic ether groups by the catalytic action of molecular chlorine

The relative ease of demethylation of lignin in the chlorination reaction has been known for a long period of time⁹. As has been recently demonstrated¹⁰ the methoxyl loss is due to the formation of methanol, which can be recovered from the bleach liquor and is quite stable to the action of molecular chlorine. Model compound studies suggest that the methoxyl groups are hydrolysed to free phenolic hydroxyl groups and methanol by the catalytic action of molecular chlorine⁸. A similar hydrolysis of ether linkages between monomeric units in lignin appears likely.

(d) Oxidation of chlorinated catechol groups to various quinone structures

These reactions are known to occur but are not advantageous for the bleaching process because the chlorinated quinones easily polymerize to larger molecular aggregates which can be removed only with difficulty.

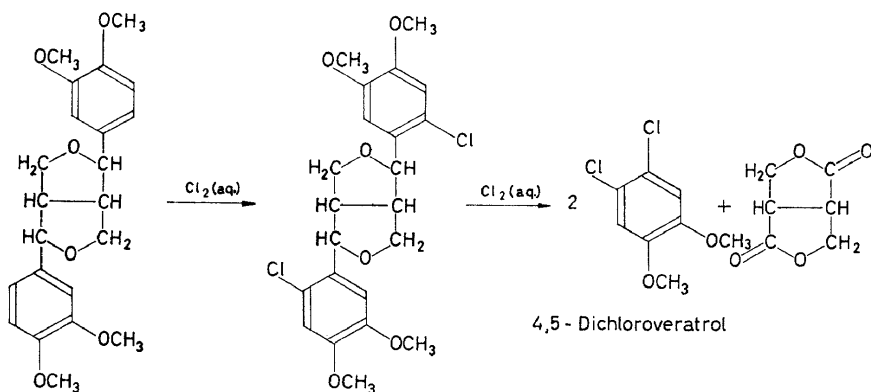


Figure 3. Chlorination of the dimethyl ether of pinoresinol

Some examples of the electrophilic displacement reactions on various model compounds are given in Figures 2 and 3. The occurrence of the displacement reaction in the end units of wood lignin has been demonstrated by converting them to tetrachloroguaiacol by chlorination in glacial acetic acid (Figure 4).

Model compound studies have shown that the hydrolysis of aromatic ether groups is subject to two inhibitive effects. Firstly, no de-alkylation reactions occur in the complete absence of water, not even in glacial acetic

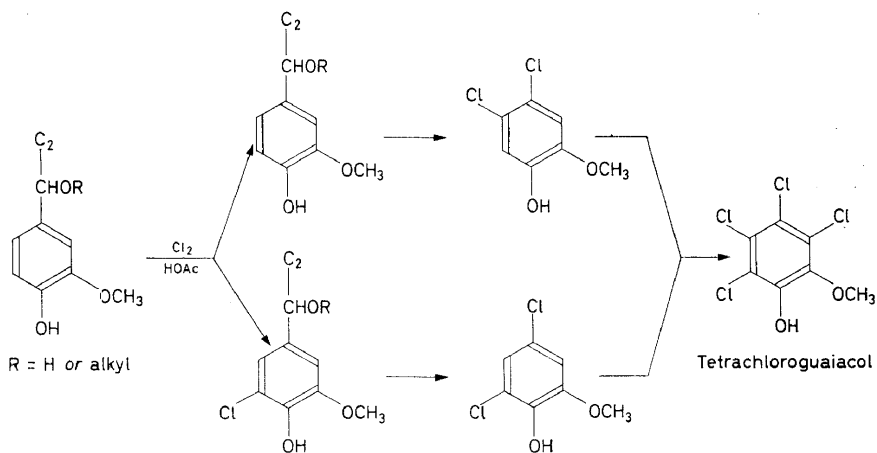


Figure 4. Reaction sequence for chlorination of end unit of spruce lignin *in situ*

acid. Secondly, the hydrolysis of veratryl-type model compounds is inhibited by two chlorine substituents *ortho* to the methylether groups. A similar inhibition effect has been observed in pyrogallol trimethylether derivatives. The effect is probably steric in nature. It is absent, however, in many compounds containing free phenolic hydroxyl groups, such as guaiacyl and syringyl derivatives.

Studies carried out on the chlorination of wood lignin and various lignin preparations suggest that both methoxyl groups and aromatic ether links are extensively hydrolysed by the catalytic action of chlorine. The reaction does not, however, reach completion, because of competitive chlorine substitution at positions 2 and 5. Figure 5, which presents the amount of liberated methanol in the chlorination of various lignins, illustrates the fact that only about 75 per cent of methoxyl groups in spruce wood and lignosulphonic acid are hydrolysed to methanol. The resistance of the remaining methoxyl groups is probably due to steric inhibition effects described above.

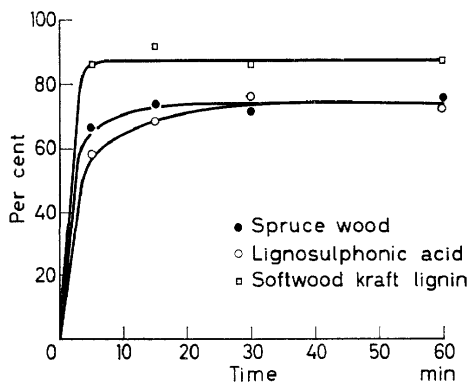


Figure 5. Production of methanol by chlorination

Figure 6 summarizes the reactions that occur in a guaiacyl propane unit during the chlorination. The reaction to occur first is chlorine substitution at either the 6- or 5-position of the nucleus. To what degree the next reaction, the electrophilic displacement of the side chain, takes place depends largely on the number of free phenolic groups and on the nature of the functional group bonded to the α -carbon of the side chain. Unfortunately, no adequate analytical means exist to determine the extent

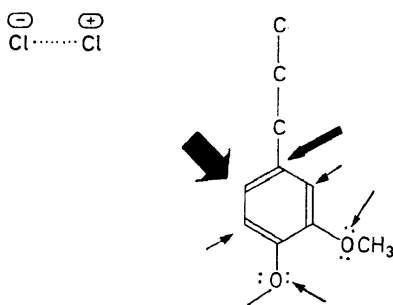


Figure 6. Sites reactive towards chlorine in a guaiacyl propane unit of lignin

of this reaction in various lignins. Since carbinol and carbinol ethers are displaced with particular ease, it would seem likely that this reaction is most extensive in the chlorination of native wood lignin and less extensive in the sulphite pulp lignin which contains sulphonic acid groups attached to the α -carbon in a substantial number of guaiacyl propane units. The hydrolysis of the methoxyl groups and 4-ether linkages proceeds to a stage that is limited by the amount of chlorine substitution at the positions 2 and 5.

It should be pointed out that side chains condensed in the 5-position are not likely to undergo electrophilic displacement reaction. Secondly formed condensed structures can consequently be expected to resist the degradative action of chlorine.

The question of the reactivity of the side chain in the chlorination still remains open. In the past, efforts have been made to determine the aliphatically bound chlorine using alkaline hydrolysis data. However, since the chlorine atoms in chlorinated quinones are easily hydrolysed by alkali, estimations of this sort are hardly reliable. Since all reactions which occur at the aromatic nucleus are very rapid, the contribution of side-chain reaction in acidic chlorination is likely to be relatively insignificant.

Hypochlorite bleaching

As pointed out earlier, the primary reactant in the hypochlorite oxidation is probably hypochlorous acid, HOCl. The information available for evaluating the degradative mechanism of hypochlorite oxidation is rather limited, and the reaction in general is probably more complicated than acidic chlorination.

In the same way as molecular chlorine, hypochlorous acid reacts as a substituting agent and scattered pieces of information in the literature¹²⁻¹⁴ indicate that it can cause electrophilic displacement reactions as well.

Some of the current ideas on the action of HOCl on phenols and phenol ethers are summarized in *Table 2*. According to de la Mare and co-workers¹⁵, HOCl itself is rather unreactive in acidic solution, but the chloronium ion formed from the reaction between hypochlorous acid and hydronium ion is a very effective substituting agent. In reactions with reactive phenols and their ethers the rate-determining step appears to be

Table 2. Hypochlorous acid as substituting agent

(1) *Acidic solution*

Rate = $k [H^+] [HOCl]$ (Reactive phenol ethers)

Reactive species Cl^+ (or H_2OCl^+)

o/p ratio higher than in case of Cl_2

(2) *Neutral and alkaline regions*

Phenol ethers unreactive

Free phenols: rate = $k [C_6H_5O^-] [HOCl]$; optimum pH = $\frac{1}{2}(pK_{C_6H_5O^-} + pK_{HOCl})$

Carbohydrates: rate probably 2nd order in $[HOCl]$

Decomposition to ClO_3^- and Cl^- : rate 2nd order in $[HOCl]$

the formation of chloronium ion, and the reaction is consequently zero order with respect to the substrate. The *o/p* ratio in substitution reactions is generally higher than in chlorinations with elemental chlorine, probably for reasons of steric nature.

In the neutral and alkaline regions, hypochlorous acid itself acts as a reactive species, but is only capable of reacting with negatively charged ions. This is indicated by the fact that most phenolic ethers are practically unreactive while free phenols are rapidly substituted according to the expression¹⁶:

$$\text{Rate} = k[C_6H_5O^-][HOCl]$$

As can be shown by a simple calculation, a maximum rate is obtained at a pH equal to the arithmetic mean of the pK values of hypochlorous acid (7.4) and the phenol. Ordinary phenols usually have a pK value of about 10. Consequently, the maximum rate region should be close to pH 9 or slightly below. With very reactive phenols, substitution reactions can be accomplished at as high a pH as 12.

These results would suggest that the etherified units in lignin might be quite unreactive in hypochlorite oxidation while the units with free phenolic hydroxyl groups should react with ease. This idea has received experimental support from the work by Richzenhain and Alfredsson¹⁷ who showed that diazomethane methylation drastically reduced the rate of hypochlorite oxidation from about 8 moles to less than 2 moles per phenyl propane unit.

Richzenhain and Alfredsson have been able to show that the oxidative degradation in dimeric model compounds can continue, under specific circumstances, from an unetherified unit to the next etherified unit.

Thus the available data suggest that the attack of HOCl on the aromatic moiety of the lignin molecule is essential for successful degradation in hypochlorite bleaching, and this, in turn, is dependent on the number of free phenolic units present. In this respect the action differs from that of

elemental chlorine which is capable of degrading etherified and unetherified units alike.

The reactivity ratio between lignin and carbohydrates in hypochlorite oxidation is of substantial interest, because it is known that the danger of cellulose degradation is more acute in hypochlorite oxidation than in acidic chlorination. It was pointed out earlier that the optimum pH for lignin is in the neighbourhood of 9, if it contains "normal" phenolic hydroxyl groups, while a maximum attack on cellulose occurs at about pH 7.0. Use of this fact is made in the pH adjustment of hypochlorite bleaching by which the degradation of cellulose can be kept at a minimum.

It appears, however, that the situation might actually be more complicated due to certain kinetic effects. At least the rapid substitution of unetherified guaiacyl propane units is first order with respect to hypochlorous acid concentration. The oxidation of cellulose which according to Herbst¹⁸ has an intermediate in common with hypochlorous acid self-decomposition, is probably second order with respect to hypochlorous acid concentration. If this is true, the lignin to carbohydrate reactivity ratio will depend, even at constant pH, on the concentration of HOCl, low concentrations favouring increased reaction with lignin.

Very little information is available to evaluate how the degradation reaction of aromatic nuclei continues after the initial chlorine substitution stage. The hypochlorite consumption curves by Richzenhain are equivalent to an oxidant consumption corresponding to the conversion of the rings to oxalic acid and various maleic acid derivatives. This appears reasonable, since both oxalic and maleic acids are relatively stable towards oxidation by hypochlorite.

BLEACHING WITH CHLORINE DIOXIDE AND CHLORITES

The inorganic system used in chlorine dioxide and chlorite oxidations is substantially more complicated than that used in aqueous chlorine solutions. It is very difficult to select proper conditions to study the specific actions of chlorine dioxide or that of chlorite alone, because the interconversion of these two oxidizing species can often not be avoided. A further complication arises from the fact that chlorine dioxide and chlorite may become reduced to elemental chlorine (or HOCl) during the oxidation. Consequently, the oxidation effects by the former species become masked by the relatively complicated reactions of the chlorine-water system.

Only few degradation products have been characterized from the oxidation of lignin with chlorite and chlorine dioxide. Pearl¹⁹ isolated 6-chlorovanillin from the filtrate of the chlorite holocellulose preparation of spruce wood. During the formation of this product the original side chain was oxidatively degraded and the aromatic ring remained intact; fumaric acid, isolated by Barton²⁰, probably derives its origin from aromatic rings. The monochloroacetic acid, isolated by the last-mentioned investigator, may again be a side-chain oxidation product.

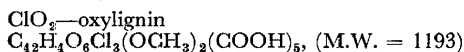
It appears, therefore, that chlorine dioxide and/or chlorites may exert oxidative attack both on the side chains as well as on the aromatic nuclei. This complex action makes the interpretation of the analytical data by

Barton²⁰ and Purves and co-workers²¹ on lignins oxidized by chlorine dioxide (*Table 3*) and chlorites somewhat difficult.

Table 3. Compositions of chlorine dioxide and chlorite lignins

Barton ²⁰ :	Chlorite lignin A	Ether-solubles
$\begin{array}{c} \text{CH}_3\text{O} \\ \text{CH}_3\text{O} \\ \text{HO} \\ \text{HO} \end{array} \begin{array}{c} \diagdown \\ \diagdown \\ \diagdown \\ \diagdown \end{array} \text{C}_{22}\text{H}_{18}\text{O}_6 \begin{array}{c} \diagup \\ \diagup \\ \diagup \\ \diagup \end{array} \begin{array}{c} \text{COOH} \\ \text{COOH} \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{COOH} \\ \text{COOH} \\ \text{Cl} \end{array}$	$(\text{COOH})_2$ <i>trans</i> -HOOCCH=CHCOOH CH_2ClCOOH

Purves *et al.*²¹:



From the analytical data shown, it can be concluded that the following gross changes take place in the lignin molecule during the oxidation:

- (i) reduction in methoxyl content;
- (ii) increase in acidic groups which may be titrated, probably carboxyl groups. Purves has pointed out, however, that these groups may consist, in part, of hydroxyl groups associated with quinone nuclei, whose chemical behaviour cannot easily be distinguished from that of carboxyl groups;
- (iii) introduction of chlorine in the molecule.

By alkaline saponification Purves *et al.* were able to almost double the number of acidic groups in their preparation; similar observations were made by Barton. This suggests that substantial amounts of lactone or ester groups might be present.

In all cases studied, the chlorine dioxide treatment results in the elimination of the 280 m μ maximum from the u.v. spectrum of lignin. This observation is generally interpreted to mean partial oxidative destruction of aromatic nuclei. Such reaction, if it occurs, would naturally account for the loss of methoxyl groups and contribute to the number of carboxyl and/or lactone groups.

This concept has received certain support from model compound studies. Already Schmidt and co-workers²² were able to show that various phenols, phenol carboxylic acids and nitrophenols are degraded to maleic and oxalic acids by chlorine dioxide. Model compounds which possess closer structural relationship with lignin were later studied by Husband, Logan, and Purves²³. It was shown by them that vanillin is converted to a crystalline compound $\text{C}_7\text{H}_5\text{O}_4(\text{OCH}_3)$. Subsequent studies²⁴ have shown that

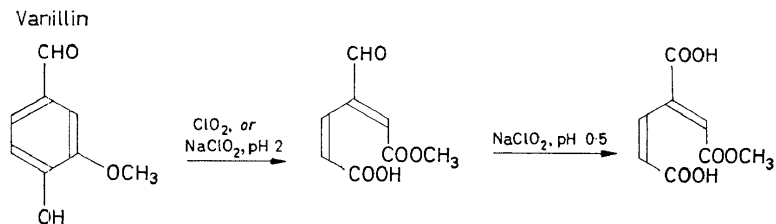


Figure 7. Oxidation of vanillin by chlorine dioxide and sodium chlorite

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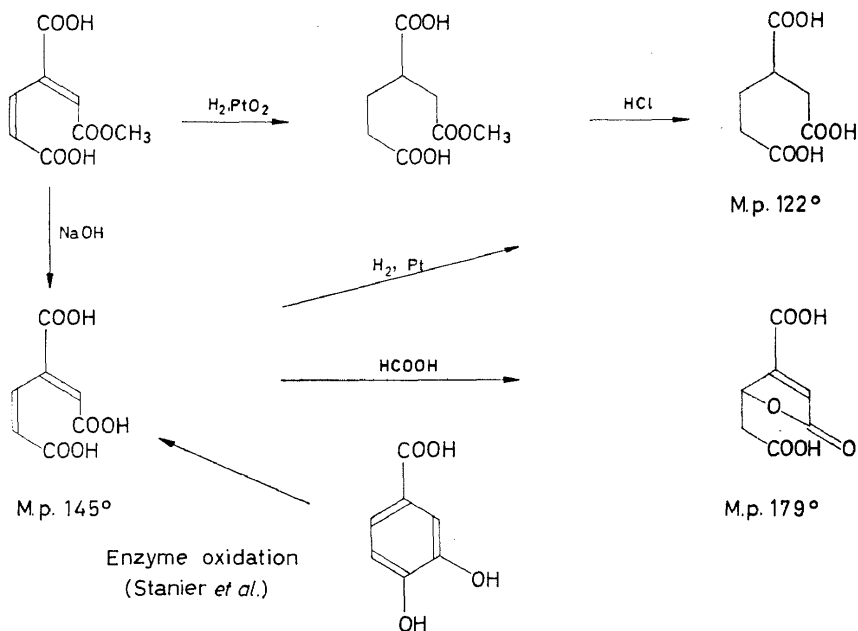


Figure 8. Reactions used for the structure assignment of β -formyl muconic acid monomethyl ester

the compound has the structure of β -formyl muconic acid monomethyl ester (Figure 7) which by chlorite oxidation is converted to corresponding muconic acid ester. Figure 8 summarizes the reactions utilized for structure assignment.

Similar ring opening reaction occurs in the chlorine dioxide (or chlorite) oxidation of vanillyl alcohol²⁵, although the reaction product is isolated in the form of a δ -lactone (Figure 9). Consequently, an oxidative ring

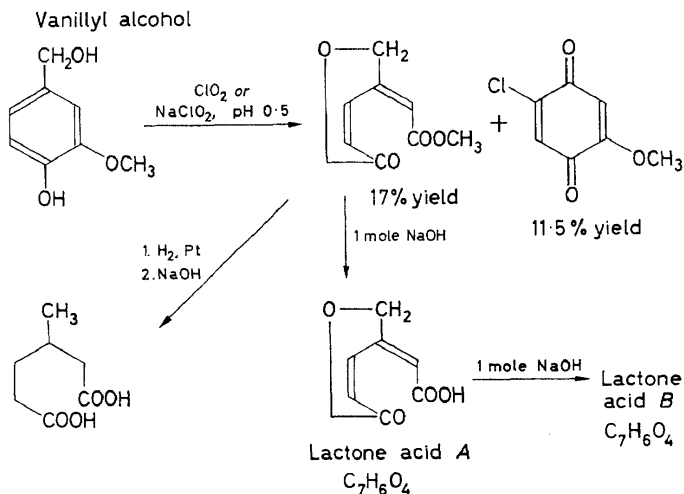


Figure 9. Oxidation of vanillyl alcohol by chlorine dioxide and sodium chlorite

opening between the carbons connected with the methoxyl and hydroxyl groups appears relatively general in guaiacyl derivatives.

2-Chloro-5-methoxybenzoquinone is an additional product from the oxidation of vanillyl alcohol. Quinones, with or without a chlorine substituent, are frequently obtained as products from the chlorine dioxide oxidation of various models²⁶.

Both in the ring opening and in the formation of methoxy quinones, the original aromatic methoxyl is converted to a less stable form which can be easily hydrolysed to methanol, while the methoxyl groups connected with unchanged aromatic nuclei are not hydrolysable under mild conditions. As a consequence, the amount of easily hydrolysable methoxyl groups can serve as a rough estimate on structures that have undergone either ring opening or conversion to methoxyquinones.

Table 4. Amount of hydrolysable methoxyl groups in model compounds and lignin preparations after oxidation with chlorine dioxide

<i>Substance</i>	<i>Methanol recovered (% of original MeO)</i>		
	<i>Formed in oxidation</i>	<i>Liberated in hydrolysis</i>	<i>Total</i>
Vanillyl alcohol	53	34	87
Veratryl alcohol	65	23	88
Lignosulphonic acid	58	7	65
Birch wood	27	7	34
Spruce wood	33	6	39

Table 4 presents some determinations of this sort carried out on model compounds and on various lignin preparations²⁵. The chlorine dioxide and chlorite oxidations were performed under mild conditions to keep at minimum the hydrolysis of the ester and quinone-methoxyl groups, as well as the further oxidation of these structures to low molecular weight compounds. The results obtained in the oxidation of vanillyl alcohol are in good agreement with the combined yields of muconic acid and methoxyquinone derivatives which were actually isolated.

The values obtained for various lignins are, however, quite low, much lower actually than the free methanol formed directly during the oxidation reaction. These results unquestionably discourage the idea of regarding the formation of muconic acid esters and methoxyquinones as major degradative processes in the chlorine dioxide oxidation of lignin. Since, however, the amount of methanol directly liberated in the oxidation is relatively large and, furthermore, the u.v. absorption of oxidized lignins indicates extensive modification of the aromatic nuclei, other reaction pathways resulting in reduced aromaticity merit consideration.

One such possibility consists of the conversion of aromatic nuclei to furan derivatives. It was shown by Pearl and Barton²⁷ that vanillin, when oxidized with sodium chlorite in acetic acid solution, gives small amounts of furan-2,4-dicarboxylic acid. Later studies²⁸ have shown that substantially higher yields of this compound (up to 15 per cent) are obtained when vanillic or

syringic acids are oxidized with aqueous chlorine dioxide or sodium chlorite. No furan-2,4-dicarboxylic acid is formed in the chlorite oxidation of β -carboxymuconic acid or its methyl ester, obviating the possibility of a common pathway.

It is obvious that data available on the chlorine dioxide and chlorite oxidations are insufficient to create more than a very preliminary picture of the chemistry of the process. The same is true, to a more pronounced degree, for the mechanism of peracetic acid delignification. Peracetic acid resembles chlorine dioxide in its capacity to oxidize phenols, catechols and their ethers to muconic acid derivatives. To what degree this similarity is related to the fact that both chlorine dioxide and peracetic acid are excellent delignifying agents, poses an intriguing problem for future research.

Anyone who visits a modern pulp bleaching plant cannot but be impressed by the scope of the operation and by the elaborate control devices. We are, unfortunately, only in the early stages of understanding the chemistry of bleaching processes, and it may be asked with good reason whether the basic knowledge of bleaching reactions lags behind the well-developed engineering of the bleaching operation.

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