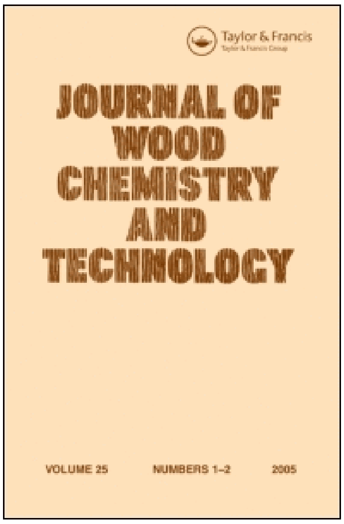

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STUDIES ON THE REACTIONS OF PHENOLIC AND NON-PHENOLIC LIGNIN MODEL COMPOUNDS WITH CHLORINE DIOXIDE

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ABSTRACT

The reaction between chlorine dioxide and four different lignin model compounds (phenolic and non-phenolic, with or without an α-hydroxyl group) are studied. The key difference with previous studies is the effective elimination of hypochlorous acid by sulfamic acid during chlorine dioxide treatment. The elimination of hypochlorous acid, an important intermediate formed during chlorine dioxide bleaching, makes it possible to study the consumption of the lignin model compounds solely as a result of the action of chlorine dioxide.

Based on almost closed mass balances for the substrate and atomic chlorine it is found that the reaction between ClO_2 and lignin model compounds is generally characterized by three independent parallel reactions:
1) demethylation, 2) formation of 2-methoxy-*p*-quinone and 3) formation of muconic acid monomethyl ester and/or its derivatives. Although, the importance of each reaction depends on the functional groups of the substrate, the demethylation reaction is the most important. It is shown that non-phenolic lignin model compounds do react with ClO_2 when ClO_2 is supplied in large excess. However at conditions representative of industrial ClO_2 application levels, only the phenolic substrates react with chlorine dioxide when both phenolic and non-phenolic lignin model compounds are present. Contrary to the previous model compound studies done without effective elimination of hypochlorous acid, no

chloroaromatic material is detected in the present investigation. This supports the view that the reaction intermediate hypochlorous acid (or chlorine) is solely responsible for the formation of chloro organic material during chlorine dioxide bleaching. Reaction mechanisms of the degradation of phenolic and non-phenolic lignin model compounds by ClO_2 are also discussed.

INTRODUCTION

Although chlorine dioxide is increasingly used during the last decade for pulp delignification, the chemical reactions between lignin and chlorine dioxide are still not fully established. Significant progress has been made towards understanding the chemistry of these reactions through studies with lignin model compounds. Previous work with lignin model compounds such as vanillin or vanillyl alcohol [1,2,3] has shown that about 30% of these lignin model compounds are converted into muconic acid monomethyl ester and chlorinated 2-methoxy-*p*-quinone during treatment with ClO_2. The results with guaiacol and catechol [4] show that the yield of *p*-quinone is 13% and 45% respectively, and with respectively only a small amount and no muconate derivatives formed. More recently, Gierer and coworkers [12,13] studied the reactions between chlorine dioxide and many different lignin model compounds and found that except for stilbenes and styrenes [13] the amount of identifiable chlorination products usually largely exceeded that of identifiable oxidation products. In both of their studies, however, no quantitative product yields were given. Therefore, from the literature it appears that the reaction between ClO_2 and lignin model compounds is characterized by the formation of muconate, *p*-quinone and chlorinated products. Since their yields are relatively low, the question arises which other reactions are responsible for the consumption of the majority of lignin model compounds.

It has been shown that hypochlorous acid is formed in a yield of 50 to 60% as a reaction intermediate during ClO_2 treatment of lignin model compounds and kraft pulp [6,7]. This result explains that a large fraction of creosol is chlorinated [5] and that chlorine substituted quinone is formed when vanillyl alcohol is treated with ClO_2 [3]. Therefore, it can be concluded that in all previous investigations with lignin model compounds the products of chlorine dioxide treatment are the result of reactions with both chlorine dioxide and hypochlorous acid (chlorine), rather than with chlorine dioxide alone.

The objective of the present work is to study the reactions of lignin model compounds with chlorine dioxide as a result of the sole action of chlorine dioxide by capturing the in-situ generated hypochlorous acid with sulfamic acid. Another characteristic of our research approach is to fully account for the disappearance of the substrate during chlorine dioxide treatment in terms of the main consumption reactions.

RESULTS AND DISCUSSION

Chlorine Dioxide Treatment of Veratryl Alcohol

It was found recently [8] that fully methylated kraft pulp was essentially unreactive when treated with ClO_2 in the presence of sulfamic acid. In order to test whether this finding could be reproduced with non-phenolic lignin model compounds, veratryl alcohol was treated with chlorine dioxide. Sulfamic acid was added prior to the addition of ClO_2 in a molar ratio of 6 times that of chlorine dioxide (see experimental procedure at the end of this paper). Separate kinetic experiments whereby the chlorine dioxide concentration was followed as a function of time showed that at a chlorine dioxide to veratryl alcohol molar ratio of 8 to 1, chlorine dioxide is fully consumed after approximately one hour. Therefore, for the experiments performed with smaller ClO_2 to substrate molar ratios, it can be concluded that 1 hour is sufficient for consumption of all the supplied chlorine dioxide. Indirectly this was confirmed by the closure of the atomic chlorine mass balance (see Table 2).

The results with veratryl alcohol are summarized in Table 1 for four different chlorine dioxide to substrate molar charge ratios. The remaining

TABLE 1: ClO_2 Treatment of Veratryl Alcohol in the Presence of Sulfamic Acid

ClO_2\substrate molar ratio	1:1	2:1	3:1	4:1
Yield (%)				
Substrate remaining	84.7	60.0	40.2	23.8
2-Methoxy-*p*-quinone (II)	0.8	1.6	2.3	3.3
δ-Lactone ester (I)	3.2	6.5	9.2	12.2
Methanol	28.2	64.6	99.8	120.8

substrate and 2-methoxy-*p*-quinone listed in Table 1 were identified by comparing the GC analysis of the reaction mixture with that of the pure compounds. The δ-lactone ester (6-hydro-5E-(methoxycarbonyl-methylene)-2-pyrone) was isolated from the reaction mixture and its structure was confirmed by ^1H NMR spectroscopic analysis. The concentrations of veratryl alcohol, 2-methoxy-*p*-quinone, δ-lactone ester and methanol in the reaction solution were determined quantitatively by GC analysis.

Table 1 shows that the consumption of veratryl alcohol is approximately proportional to the chlorine dioxide charge. A small amount of 2-methoxy-*p*-quinone is formed, and somewhat more of the substrate is converted to the δ-lactone ester. The dominant identified product, however, is methanol. Since the formation of quinone (II) and δ-lactone ester (I) requires the removal of one of the two methoxyl groups from veratryl alcohol, 1 mole of methanol must be formed for each mole of both products produced. If it is now assumed that 2-methoxy-p-quinone and δ-lactone ester are the only partially demethylated products formed during chlorine dioxide treatment, then substraction of the yields of quinone (II) and lactone ester (I) from that of methanol formed (the last line of Table 1), will give the fraction of substrate from which both methoxyl groups

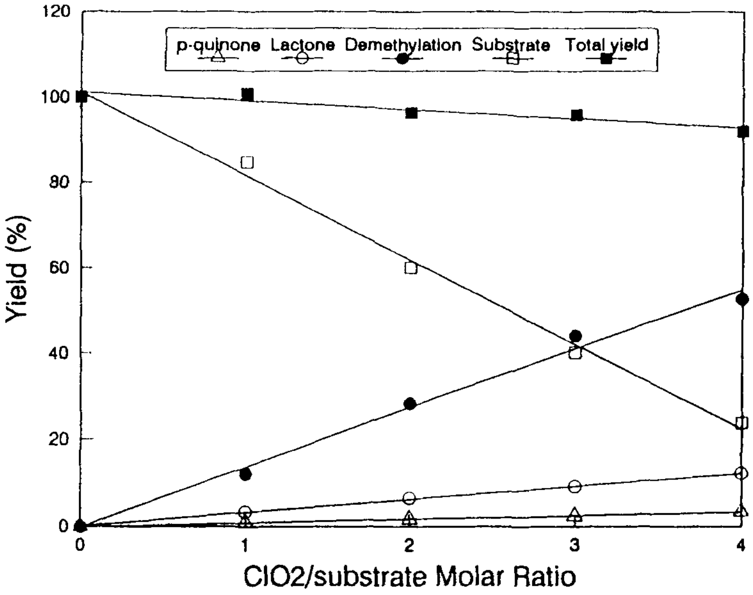


Fig.1 Development of the main reactions and substrate mass balance during ClO_2 treatment of veratryl alcohol in the presence of sulfamic acid

are removed as methanol. This reaction pathway will now be defined as demethylation. Because two moles of methanol are formed for each mole of substrate consumed by demethylation, the demethylation yield in percent, based on the substrate, is half of the difference between the methanol yield and the sum of the yields of 2-methoxy-*p*-quinone and δ-lactone ester in Table 1. When the yields of 2-methoxy-*p*-quinone (II), δ-lactone ester (I), demethylation and the remaining substrate are plotted in Figure 1, it can be seen that the overall substrate mass balance is closed over the whole range of ClO_2/substrate molar ratios studied (the top line in Figure 1). This indicates that the reaction between ClO_2 and veratryl alcohol can be quantitatively described by three parallel reaction pathways: demethylation, formation of 2-methoxy-*p*-quinone (II) and formation of δ-lactone ester (I) (Figure 2)

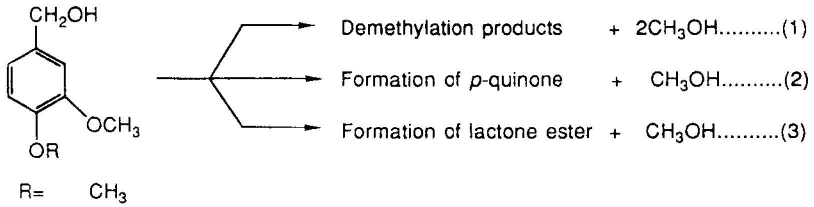


Fig. 2 The main reactions during ClO_2 treatment of veratryl alcohol in the presence of sulfamic acid

The relative reaction rate of these three reactions is approximately as follows;

reaction 1: reaction 2: reaction 3 = 16:4:1

independent of the substrate consumption as shown by the straight lines in Fig. 1.

The various inorganic chlorine containing species were also determined using analytical techniques described earlier [7]. The dissolved organic chlorine content in the reaction mixture was measured using the AOX technique [7]. It was found that the reaction product 2-methoxy-*p*-quinone interfered with the titration for the determination of hypochlorous acid captured by sulfamic acid. However, it was found experimentally that 2-methoxy-*p*-quinone reacts quantitatively with potassium iodide, and since the amount of 2-methoxy-p-quinone is known from GC analysis, a correction for its presence can be made. The corrected hypochlorous acid yield, together with that of other chlorine containing species are shown in Table. 2. It can be seen that the overall atomic chlorine mass balance is reasonably well closed for all ClO_2 to substrate molar ratios. No detectable amount of chlorate is formed, confirming the earlier reported results for ClO_2 treatment of kraft pulp [8] that the chlorate formation is minimal when hypochlorous acid is captured. The organic chlorine formation, determined collectively as AOX in solution, is very low. This result is quite different from that of the literature [2,3,5], which shows that large amounts of chlorinated quinone

TABLE 2: Atomic Chlorine Mass Balance when Veratryl Alcohol is Treated with ClO_2 in the Presence of Sulfamic Acid

ClO_2/subs molar ratio	Yield (%)					Cl mass balance
	Cl^-	ClO^-	ClO_2^-	ClO_3^-	Org-Cl	
1	21.2	56.4	20.6	NI	~ 0.7	98.9
2	18.5	57.4	20.3	NI	~ 0.6	96.8
3	19.8	56.2	19.2	NI	~ 0.6	95.8
4	20.7	55.9	18.9	NI	~ 0.8	96.3

NI: peak too small to be integrated (<0.2%)

and chlorinated substrate are formed during ClO_2 treatment of lignin model compounds. The reason for this difference is that the reaction intermediate, hypochlorous acid, is captured by sulfamic acid in the present case. This further confirms our previous finding that hypochlorous acid is mainly responsible for the organic chlorine formation during ClO_2 bleaching of kraft pulp. It also explains the experimental results of Dence et al.[3] that no chlorinated *p*-quinone is formed when α-methyl vanillyl alcohol is reacted with chlorite, while significant amounts of chlorinated *p*-quinone is formed during ClO_2 treatment of the same substrate. In the former case, hypochlorous acid reacts preferentially with chlorite, while in the latter case hypochlorous acid reacts with α-methyl vanillyl alcohol via electrophilic substitution. Another recent confirmation that the formation of chlorinated products is inhibited when hypochlorous acid is captured was presented by Ljundgren et al. [15]. They reacted monomeric and dimeric non-phenolic lignin model compounds (1-veratryl-propanol and veratryl-ethyleneglycol-ß-guaiacyl ether respectively) with chlorine dioxide. Without the presence of sulfamic acid the yield of monochloro-substituted substrate was about 20 and 30% respectively, while with sulfamic acid no chlorinated compound was found at all.

TABLE 3: ClO_2 Treatment of Veratrol in the Presence of Sulfamic Acid

ClO_2/substrate molar ratio	1:1	2:1	3:1	4:1
Yield (%)				
Substrate remaining	90.0	83.6	63.8	58.8
2-Methoxy-*p*-quinone (II)	3.0	6.2	8.9	13.2
Methanol	17.2	34.8	56.4	72.4

Chlorine Dioxide Treatment of Veratrol

The experiments with veratrol were performed under the same conditions as those of veratryl alcohol. The yields of the remaining substrate and reaction products are shown in Table 3.

In comparison with veratryl alcohol more substrate remains and less methanol is formed with veratrol at the same ClO_2 charge. This indicates that the hydroxymethyl group increases the reactivity of veratryl alcohol towards chlorine dioxide. Another characteristic of the reaction between veratrol and chlorine dioxide is that no δ-lactone ester is formed. This suggests that the formation of lactone ester is limited to substrates containing a free α-hydroxyl groups. Following the same calculation procedure as for the chlorine dioxide treatment of veratryl alcohol one can generate an overall substrate mass balance, as shown in Fig. 3. In this figure, the substrate consumption can be quantified by two reactions: the formation of 2-methoxy-*p*-quinone and demethylation, respectively reactions 3 and 1 in Fig. 2. Of these, demethylation remains dominant, accounting for about 70% of the veratrol consumed. The closed substrate mass balance and straight line relationships with the ClO_2/substrate molar ratio in Fig. 3 indicates that the reaction between veratrol and ClO_2 can also be described by two parallel reaction pathways: i.e. that of demethylation and quinone formation.

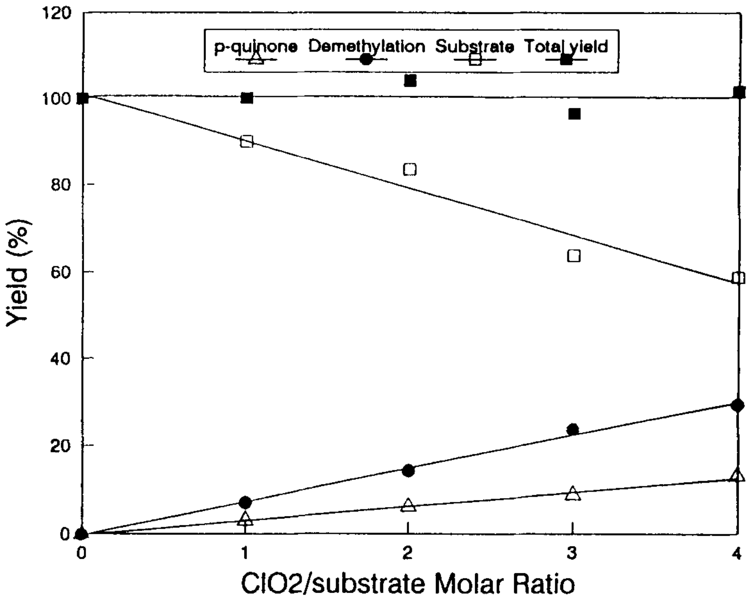


Fig. 3 **Development of the main reactions and substrate mass balance during chlorine dioxide treatment of vetatrol in the presence of sulfamic acid.**

Chlorine Dioxide Treatment of Vanillyl Alcohol

Since free phenolic compounds react more readily with ClO_2, the ClO_2 charge to model compound vanillyl alcohol is reduced by a factor of two compared to that used for non phenolic model compounds presented earlier. The results are summarized in Table 4.

The products generated in the presence of sulfamic acid can still be identified as demethylation, formation of 2-methoxy-*p*-quinone and formation of δ-lactone ester. Since the substrate mass balance is nearly closed, one can conclude that the reaction also follows the three parallel reaction pathways as described in Fig. 2. The yield ratios are now 2: 1.25 :1 respectively. The obvious difference, with the results obtained for veratryl alcohol, is that the present yields of both

TABLE 4: ClO_2 Treatment of Vanillyl Alcohol in the Presence of Sulfamic Acid

ClO_2 /substrate molar ratio	0.5:1	1:1	1.5:1	2:1
Yield (%)				
Substrate remaining	66.3	34.6	10.6	0
2-Methoxy-*p*-quinone (II)	6.2	14.3	20.1	23.6
δ-Lactone ester (I)	7.8	17.8	23.9	29.4
Methanol	12.5	25.6	39.4	47.2
Substrate mass balance	92.8	92.3	94.0	100.2

quinone and lactone ester are higher. This means that even though a phenolic hydroxyl group enhances all three reactions, the formation of *p*-quinone and δ-lactone ester are more pronounced. Table 4 also shows that at a chlorine dioxide to substrate molar ratio of 2, no substrate remains after one hour at room temperature while the methanol recovery is 47.2%. This compares well with the result obtained by Dence et al.[3] that 53% of the methoxyl groups are converted to methanol when vanillyl alcohol was treated at a ClO_2 to substrate molar ratio of 3 for 2 hours. The larger methanol yield reported by Dence et al.[3], is probably due to the contribution by hypochlorous acid (chlorine) which was not captured by sulfamic acid as in our experiments. The small difference between 47.2% and 53% also confirms the previous finding for chlorine dioxide treatment of kraft pulp [9] that chlorine dioxide is the dominant contributor to demethylation during ClO_2 bleaching.

The atomic chlorine mass balance is summarized in Table 5. Similar to the previous results for veratryl alcohol, hypochlorous acid is the dominant species and no detectable amount of chlorate is measured, while the formation of

TABLE 5: Atomic Chlorine Mass Balance when Vanillyl Alcohol is Treated with ClO_2 in the Presence of Sulfamic Acid

ClO_2/Subs. Molar Ratio	Yield (%)					Cl mass balance
	Cl^-	ClO^-	ClO_2^-	ClO_3^-	Org-Cl	
0.5	20.2	68.9	6.9	NI	~ 0.5	96.5
1	20.3	69.1	5.4	NI	~ 0.5	95.3
1.5	21.0	69.9	4.8	NI	~ 0.5	96.2
2.0	20.9	71.2	3.6	NI	~ 0.5	96.2

NI, peak too small to be integrated (<0.2%)

organic chlorine is negligible. This again supports the results obtained for chlorine dioxide treatment of kraft pulp with respect to chlorate formation [14] and organic chlorine formation [7]. Compared to veratryl alcohol, the hypochlorous acid yield for vanillyl alcohol is about 15% (absolute) higher while the chlorite yield for vanillyl alcohol is much lower. The chloride yield is approximately the same for both substrates.

Chlorine Dioxide Treatment of Creosol

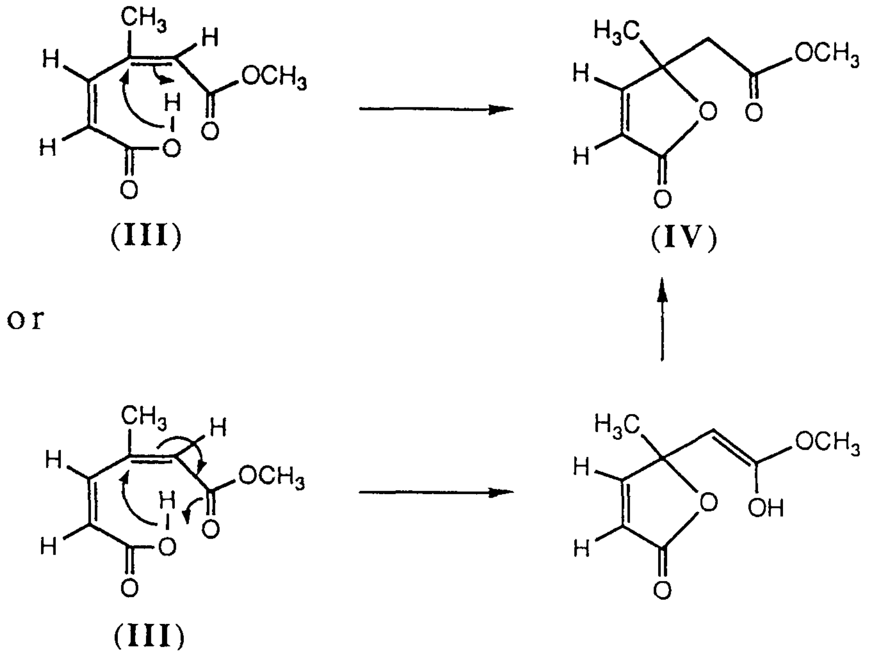
Since free phenolic lignin with a hydroxyl group in the α-carbon position, represented by model compound vanillyl alcohol are relatively unimportant in residual lignin, it is of interest to examine the reaction behaviour of chlorine dioxide treatment of a free phenolic lignin model compounds which do not contain a hydroxyl group in the α-carbon position. As representative of this type of lignin the lignin model compound creosol was investigated.

The results in Table 6 show that demethylation is the only identifiable reaction between creosol and ClO_2. GC analysis clearly shows that neither 2-methoxy-*p*-quinone nor δ-lactone ester are formed over the entire range of ClO_2

TABLE 6: ClO_2 Treatment of Creosol in the Presence of Sulfamic Acid

ClO_2/substrate molar ratio	0.5:1	1:1	1.5:1	2:1
Yield (%)				
Substrate remaining	73.6	48.3	19.2	0
Methanol	22.0	45.8	66.6	83.9
Substrate mass balance	95.6	94.1	85.8	83.9

charge. However, the substrate mass balance in Table 6 also shows that demethylation can not account for all the substrate consumed. This indicates that other reaction(s) could possibly be involved. This is further supported by the fact that the substrate mass balance deficit is approximately proportional to the ClO_2 charge. Therefore, further experiments were performed to identify other reaction products. ^1H NMR analysis of the methylene chloride extract of the reaction mixture clearly showed the presence of methoxyl containing compounds when the substrate was completely consumed at a ClO_2/substrate molar ratio of 2.0. ^1H NMR analysis suggests that these methoxyl containing compounds were (2Z,4Z)-3-methyl muconic acid monomethyl ester (III) and 5-methyl-5-(methoxy carbonylmethyl)-2(5H)-furanone (IV) and that their yields were approximately 9% and 8% respectively. The γ-lactone ester (IV) is likely generated from the acid ester (III) by a ring closure reaction (see Scheme 1). Experimental evidence for this conversion is that the acid monoester (III) was completely converted into the γ-lactone ester (IV) after being kept at room temperature for a few days. Among many reaction products compounds III and IV were also recently identified by Brage et al.[12] who treated creosol with ClO_2 without the presence of sulfamic acid. Therefore, it seems likely that for the present reaction system the deficit of the substrate mass balance in Table 6 is the result of the formation of muconic acid monomethyl ester.



Scheme 1

The results in Table 6 also show that less creosol is consumed compared to that obtained by Nonni and Dence [5]. This could be attributed to the rapid and significant chlorine substitution of creosol to chlorocreosol in their case, while in our experiments the presence of sulfamic acid prevented the formation of any significant amount of chlorine substituted products.

Chlorine DIoxide Treatment of Mixture of Veratryl Alcohol and Vanillyl Alcohol

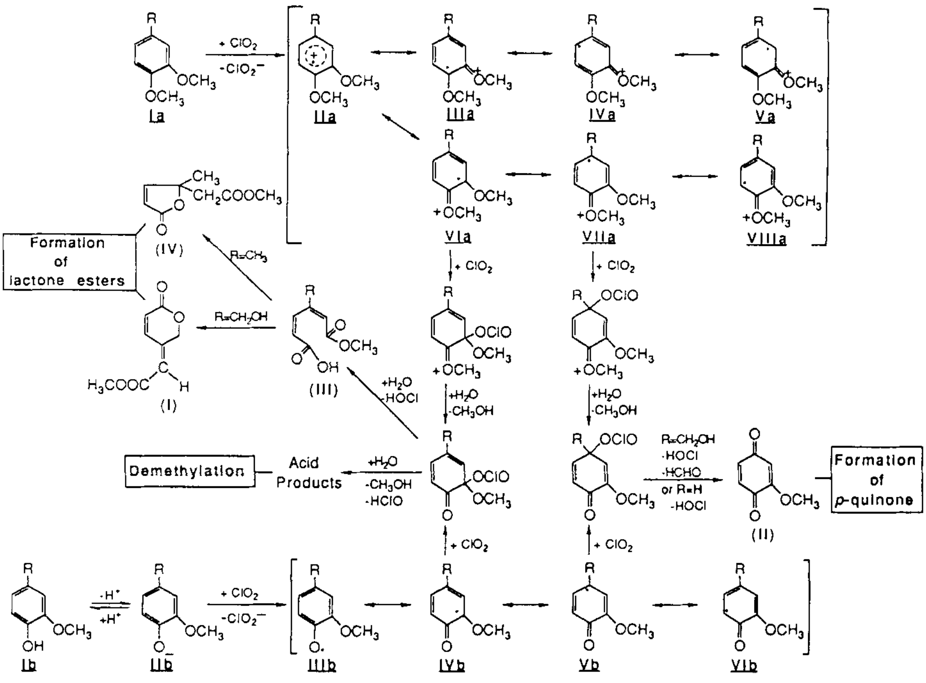
In this study it has been shown that the reaction of ClO_2 with non-phenolic lignin model compounds, such as veratrol and veratryl alcohol does proceed to a certain extent even with the presence of sulfamic acid. This is significant because Ljundgren et al.[15] report that with somewhat different non-phenolic lignin model compounds, 1-veratryl-propanol and veratryl-ethyleneglycol-ß-guaiacyl ether, the substrate is hardly consumed when sulfamic acid is present. Also the present results obtained with the non-phenolic lignin model compounds appear to be in contradiction with the finding that fully methylated kraft pulp is essentially unreactive towards chlorine dioxide at practical operating conditions when sulfamic acid is present [8,9]. In order to determine the relative reactivity of the phenolic and non-phenolic model compounds an experiment was done with both compounds present in the reaction mixture, and when the ClO_2 charge is similar to that of pure ClO_2 bleaching in industry.

A mixture of equal moles of veratryl alcohol and vanillyl alcohol was subjected to ClO_2 treatment at molar ratio of ClO_2 to veratryl alcohol of 1.50 (corresponding to D100 bleaching at an active chlorine charge factor of 0.22 at 30 kappa no.). After one hour, it was found that 87.4% of vanillyl alcohol is consumed while 98.1% of veratryl alcohol still remains. The consumption of 87.4% vanillyl alcohol is only slightly smaller than that of 89.4% when no veratryl alcohol is present (Table 4). Gierer et al. [12] also reported that creosol reacts with chlorine dioxide seven orders of magnitudes faster than 4-methyl veratrol (the reaction constants are 8.9 x 10^3 $M^{-1}S^{-1}$ and 6 x $10^{-4}M^{-1}S^{-1}$ respectively). This suggests that under the conditions encountered in industrial practice, only phenolic lignin structures are reactive towards chlorine dioxide.

Reaction Mechanism

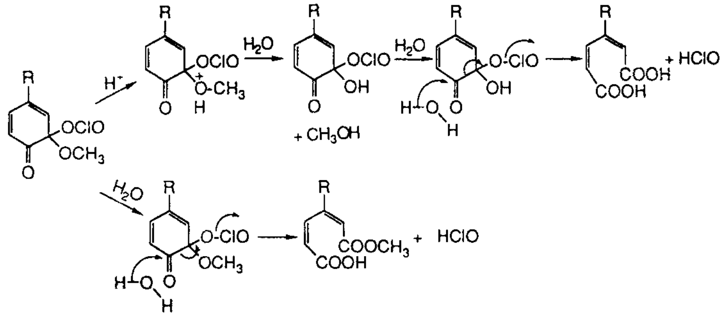
It has been proposed that the initial step of the oxidation of lignin model compounds by chlorine dioxide involves an one-electron transfer from the aromatic ring of non-phenolic structures to form an aryl cation radical [12] or from a phenolate hydroxyl group to generate the phenoxy radical respectively [3,4,6,8]. The series of resonance structures, formed in the former case are represented by IIa - VIIIa (see Scheme 2), while in the latter they are depicted by IIIb - VIb (see Scheme 2).

Demethylation and the formation of lactone esters are obtained via resonance structures VIa and IVb, which are further attacked by chlorine dioxide



Scheme 2

to form a chlorite ester structure. The following hydrolysis of the chlorite ester can proceed in two parallel reactions:



(1)

(2)

Demethylation is the result of acid hydrolysis with the formation of muconic acid derivatives, while in reaction 2, attack of water on the keto substituted carbon atom leads to the formation of muconic acid monomethyl ester derivatives, which are the precursors of the detected lactone ester. The formation of *p*-quinone is relatively small because it is formed from the less stable resonance structures, VIIa or Vb where the substituent R is a free α-hydroxyl group or hydrogen. As confirmed by our experimental results, its formation is only possible if the substituent R is a free α-hydroxyl group or hydrogen.

CONCLUDING REMARKS

In the present study, the reaction between lignin and chlorine dioxide was studied at the model compound level. Two types of lignin structures were investigated: those with a phenolic or non-phenolic character,and those with the presence or absence of an α-hydroxy group in the side chain.

The uniqueness of the present research compared to that of previous chlorine dioxide studies of lignin model compounds is that almost all of the consumed substrate has been accounted for and the consumption reaction path is defined. Also and equally important, with the capture of hypochlorous acid by sulfamic acid, chlorine dioxide is the only effective reagent in the present investigation.

The result of this study shows that under practical conditions chlorine dioxide only reacts with phenolic lignin structures. For all the four lignin model compounds investigated, the substrate consumption can be generally characterized by three independent, parallel reactions: demethylation, formation of 2-methoxy-*p*-quinone, and formation of lactone derivatives. The relative contribution of each reaction depends on the functional groups of the substrate. However, in all cases demethylation is the most important reaction. Formation of 2-methoxy-*p*-quinone only takes place if the side chain of the aromatic structure possesses an α-hydroxyl group. Since it is known that the fraction of lignin with α-hydroxyl groups entering the bleach plant is rather small, the implication is that delignification by chlorine dioxide in practice is mostly accomplished through a process whereby methanol is directly produced, i.e. the so called demethylation reaction pathway in the present study.

The limited reaction between ClO_2 and phenolic lignin model compounds can be explained by the formation of cation radicals, first proposed by Gierer et al. [12,13]. The results of this study also show the much greater reactivity of free phenolic lignin units compared to their etherified counterparts, and confirm that in practice chlorine dioxide itself reacts only with phenolic lignin. However, ClO_2 can indirectly react with non-phenolic lignin after the formation of phenolic groups by hydrolysis through the catalytic action [16] of the chlorine dioxide reaction intermediate, hypochlorous acid.

Contrary to earlier work with lignin model compounds no chloroaromatic compounds were detected by gas chromatographic analysis in the present study. This is further supported by the fact that organically bound chlorine, characterized as AOX, is negligible in all cases. Therefore, it confirms the previous finding [7] for chlorine dioxide bleaching of kraft pulp, that the in-situ generated hypochlorous acid is responsible for the formation of organic chlorine.

EXPERIMENTAL

Model Compounds

Veratryl alcohol, vanillyl alcohol, veratrol and creosol are commercially available.

The conditions of the gas chromatographic analysis for the determination of organic products and methanol are the same as in ref. 10.

NMR spectroscopic measurements were carried out at room temperature using a Varian XL 200 or XL 300 NMR spectrometer and tetramethylsilane as an internal standard.

Chlorine Dioxide Treatment

The model compounds (0.2 m mole) were first dissolved in 10 ml 1,4-dioxane, then 1 ml of this mixture was transferred to a 50 ml flask with a ground glass stopper. The ClO_2 solution was prepared at a concentration such that the required volume was less than 10 ml. Sulfamic acid was added prior to the addition of the ClO_2 solution in a molar ratio of 6 times that of chlorine dioxide. Then the exact amount of deionized water was added to a total liquid volume of 40.0 ml. The quantity of chlorine dioxide solution was varied to obtain ClO_2/substrate molar ratios up to a maximum of 4. The reaction mixture was magnetically stirred at room temperature for one hour. At the end of this period, 1 ml sample was taken for ion chromatographic analysis of chloride and chlorate according to the method described earlier [7]. Another 1 ml sample was taken and added to a solution containing 0.05 g of potassium iodide in order to stop further reaction. This sample was then used for the determination of methanol. The remaining reaction solution was immediately subjected to a nitrogen purge, immersed in an ice bath. Then, 10 ml sample was analyzed for chlorite and hypochlorous acid which was captured by sulfamic acid according to the titration method established earlier [7]. The reaction solution was extracted with ether or $CHCl_3$ and the extracts were then ready for gas chromatographic analysis.

Isolation of 6-hydro-5E-(methoxycarbonyl-methylene)-2-pyrone(I) and 2-methoxyl-p-benzoquinone(II)

The reaction solution of vanillyl alcohol with chlorine dioxide at a ClO_2/substrate molar ratio of 2.0 was extracted with methylene chloride, washed with water, dried over anhydrous sodium sulfate and evaporated to dryness. The yellow residue was dissolved in $CDCl_3$, and analysed by ^1H NMR spectroscopy. The ^1H NMR spectrum indicated that the residue consisted of two components, I (yield 26%) and II (yield 22%). If the methylene chloride extract was treated with sodium bisulfite, a colorless crystalline product II was isolated. ^1H NMR data for compound I, δ(ppm): (8.35 (dd, 1H, J = 10.1 Hz and 1.0 Hz, 3-H), 6.22 (dd, 1H, J=10.1 Hz and 1.7 Hz, 4-H), 5.96 (m, 1H, $=CH\text{-}COOCH_3$), 5.04 (d, 2H, J=1.7Hz, CH_2), 3.82 (s, 3H, OCH_3); for compound II, δ(ppm): 6.74 (d, 2H, 5-H and 6-H), 5.97 (s, 1H, 3-H), 3.85 (s, 3H, OCH_3).

(2Z, 4Z)-3-methyl muconic acid monomethyl ester (III)

^{1}H NMR data: δ(ppm): 7.15 (dd, 1H, J=12.3 Hz and 1.0 Hz,4-H), 5.83 (dd, 1H, J=12.3 Hz and 0.8 Hz, 5-H), 5.72 (m, 1H, 2-H), 3.64 (s, 3H, OCH_3), 2.02 (s, 3H, CH_3).

5-methyl-5-(methoxycarbonyl-methyl)-2(5H)-furanone (IV)

^{1}H NMR data: δ(ppm): 7.64 (d, 1H, J=5.6 Hz, 4-H), 6.01 (d, 1H, J=5.6 Hz, 3-H), 3.61 (s, 3H, OCH_3), 2.87 (d, 1H, J=15.6Hz, α-H), 2,64 (d, 1H, J=15.6Hz, α^1-H), 1.51 (s, 3H, CH_3).

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