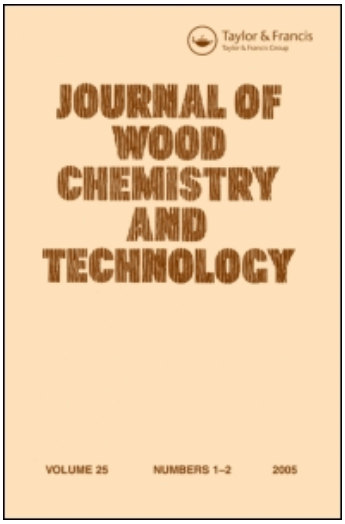

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PULPING CATALYSTS FROM LIGNIN (5). NITROGEN DIOXIDE OXIDATION OF LIGNIN MODELS TO BENZOQUINONES

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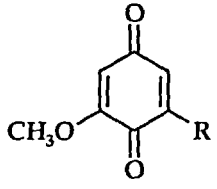
ABSTRACT

Several syringyl lignin models have been oxidized to 2,6-dimethoxy-*p*-benzoquinone (DMBQ) in high yields with nitrogen dioxide (NO_2) in methanol solvent. The yields of DMBQ were high for syringyl alcohol, syringaldehyde, and disyringyl methane and moderate for several other phenolic syringyl models. Benzoquinones were not formed from non phenolic substrates. The yields were slightly improved by the presence of N-hydroxysuccinimide. Guaiacyl lignin model compounds gave low benzoquinone yields; the major products were C-5 nitro substituted compounds. A radical mechanism is proposed to explain the observed results.

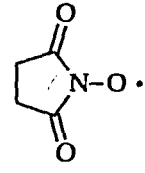
INTRODUCTION

We have been investigating ways to convert lignin to anthraquinone-type pulping catalysts.[2] The oxidation of certain lignin model compounds with Fremy's salt, $(KO_3S)_2N\text{-}O\bullet$, can provide high yields of methoxy-sub-

stituted benzoquinones (1 and 2) in many cases;[2a] the benzoquinones can be treated with isoprene to give 2,6- and 2,7-dimethylanthraquinone.[2b]



1, R = H (MMBQ)
2, R = OCH_3 (DMBQ)



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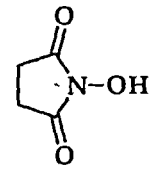

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While Fremy's salt may be a good oxidizing agent for converting lignin and related structures to benzoquinones, it has some drawbacks: its expense and a reactivity that is unpredictable when used on large scale.[3] Therefore, we sought another oxidizing agent that was more suitable for commercial use and might also initiate reaction by removal of a phenolic hydrogen.[2a] The radical species 3 derived from commercially available N-hydroxysuccinimide (NHS, 4) looked to be a reasonable candidate; it too is a nitroxide similar to Fremy's salt. We anticipated that the radical (3) would react with suitably substituted phenols to generate phenoxy radical 5, which in turn would combine with radical 3 to give adduct 6 (Figure 1). Decomposition of adduct 6 should give benzoquinones 1/2, amide 7, and the oxidized side chain.

A potential way to generate the NHS radical might be to treat NHS with nitrogen dioxide (NO_2), a natural radical. This led to the hypothesis that the combination of NO_2/NHS might oxidize 4-substituted phenols to benzoquinones. However, we soon realized that NO_2 was an effective oxidizing agent in the absence of NHS. This may because NO_2 is capable of abstracting hydrogen atoms from phenols,[4] and reacting with phenolic radicals. The present investigation examines the potential scope of NO_2 oxidations with lignin-related compounds, and the effects of NHS and other variables on the oxidations.

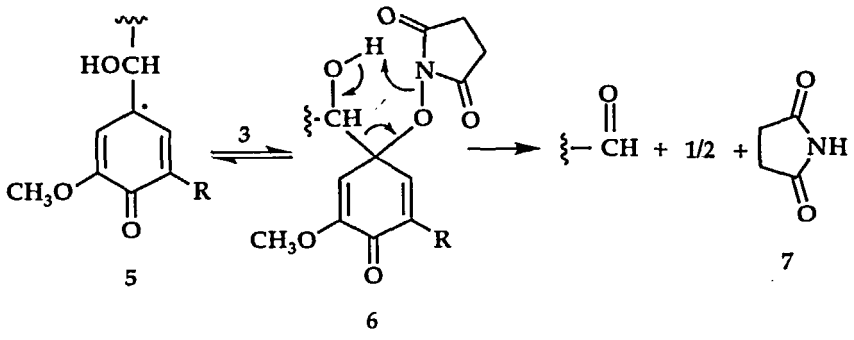
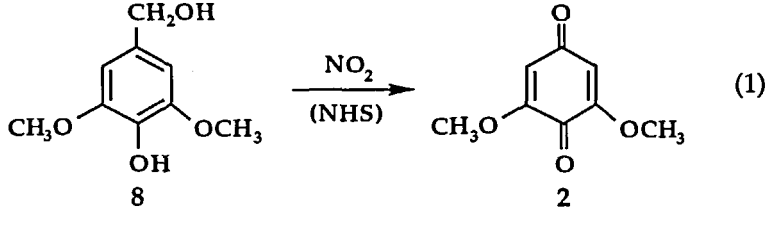


Figure 1. Projected phenol oxidation chemistry for NHS.

RESULTS AND DISCUSSION

Solvent Effects on NO_2 Oxidations

We began our studies by examining the NHS/NO_2 reactions of syringyl alcohol (8). The latter compound is representative of the terminal syringyl units found in hardwood lignins.[5] The reaction of interest is given in Equation 1.



(1)

A summary of the results of a reaction optimization study is given in Table 1. Optimum reaction conditions for the conversion of syringyl alcohol (8) to 2,6-dimethoxybenzoquinone (DMBQ, 2) were 5-6 equiv. of NO_2 and 2-3 equiv. of NHS in methanol for 30 minutes. Under these conditions, the reaction mixture turned yellow after 10 minutes and a precipitate

Table 1. DMBQ Yields from NO_2 oxidations of syringyl alcohol (8) in various solvents after 30 min reaction at room temperature.

Solvent	DMBQ (%)[a,b]	NHS[c]
Methanol (anhydrous)	87, 86, 89[d], 80[e]	+
	81, 80, 81	-
2% Aq. Methanol	76	+
4% Aq. Methanol	76	+
20% Aq. Methanol	60[e], 63[e,g]	+
20% Aq. Methanol	55[e,f]	-
40% Aq. Methanol	53[e]	+
Ethanol (anhydrous)	25[e], 22[e,f], 25[e,g]	+
20% Aq. Ethanol	24[e]	+
Ethylene Glycol	33[d], 14[e]	+
Water	25[h]	+
Ethyl Acetate	18[d]	-
DMSO	14	-
Diethyl ether	13	-
Chloroform	10[d]	+
1,4-Dioxane	2	-
3-Methylbutanone	5	-
Acetonitrile	0	+

[a]Conditions (unless stated differently): 100+ mL headspace; 5-6 eq. of NO_2; 2 mL of solvent. [b]Yield based on direct HPLC analysis of reaction mixture using an external standard. [c]2-3 eq. when used (+). [d]GC yield for 4 mL of solvent, 2.5 eq. NO_2, 90 min, and anthraquinone as an internal standard. [e]2.5 mL headspace; 5-6 eq. of NO_2; 1 mL of solvent. [f]15 min oxidation period. [g]60 min oxidation period. [h]Isolated yield.

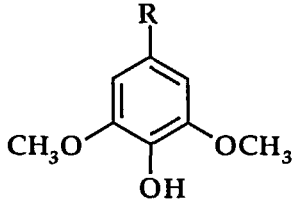
(DMBQ) formed. Addition of chloroform (to dissolve the DMBQ) and gas chromatography (GC) analysis of the resulting mixture showed DMBQ as the principal product.

The superiority of methanol as a solvent is probably related to the fact that DMBQ is not very soluble in methanol; since the formation of adduct 6 is likely to be reversible, precipitation would drive the reaction to completion and reduce secondary reactions. Methanol is known[6] to react with

NO_2 at room temperature to give MeONO and HNO_3 - possibly MeONO is a reactive oxidant. Ethanol was a less effective solvent, as were water-alcohol mixtures and nonhydroxylic solvents.

Effects of NHS on NO_2 Oxidations

No noticeable reaction occurred when syringyl alcohol was stirred for several hours with 2 equiv. of NHS; however, addition of NO_2 led to the immediate production of DMBQ. In contrast, oxidation was observed in the absence of NHS (Table 1). The yields of DMBQ from syringyl alcohol oxidation dropped by only ~7% in the absence of NHS (88% → 81% and 62% → 55% for methanol and 20% aq. methanol, respectively). Raising the ratio of NHS to syringyl alcohol from 2:1 to 4:1 in the presence of 4 equiv. of NO_2 dropped the yield of DMBQ from 89% to 40%. Consequently, there is an optimum quantity of NHS (~2 equiv.) that leads to the best yields of DMBQ. Similar trends have been seen in the case of oxidation of syringaldehyde (9).[7] The role of NHS in the NO_2 oxidations will become clearer in a subsequent publication.[8] The yields of DMBQ from model compounds and lignin[7] oxidations are improved by the addition of moderate amounts of NHS.



9, R = CHO
10, R = CH_2OCH_3

The oxidation of syringyl alcohol with varying amounts of NO_2 in the absence of NHS was also examined (Table 2). In these reactions an addition product, 2,6-dimethoxy-4-methoxymethylphenol (**10**), was also identified. The data given by the first three entries in Table 2 suggest that com-

Table 2. Effect of NO_2 concentration on the oxidation of syringyl alcohol in methanol.[a]

NO_2 (equiv.)	DMBQ (%)	10 (%)
0.27	25	12
0.50	49	5
0.74	72	2
1.00	62	2
1.50	51	5
2.00	63	7

Table 3. Effect of syringyl alcohol (8) concentration in methanol with 4 equiv. of NO_2 in the absence of NHS.

8 (mM)	DMBQ (%)
125	69
63	62
42	68
31	64

plete oxidation requires one equivalent of NO_2 with respect to the starting material. At higher concentrations the yields decreased somewhat, presumable due to decomposition of DMBQ.

Effects of Other Variables on NO_2 Oxidation Yields

Substrate concentration has been found to have no significant effect on the yield of the desired product (Table 3). Optimum reaction times depend on the substrate: ~30 minutes for syringyl alcohol and ~3 hours for syringaldehyde.

We were curious to see what influence base would have on DMBQ yields. The autoxidation of phenols occurs more readily with phenolate ions than with neutral phenols.[9] However, the NO_2 oxidation of syringyl alcohol in aqueous NaOH or $NaOCH_3/HOCH_3$ gave no more than a 10% yield of DMBQ, considerably below the typically 87-89% yield.

Table 4. DMBQ yields as a function of air removal and the presence of NHS on the 2 hr NO_2 reaction of syringyl alcohol in methanol.

Air Removal Method	NO_2 (equiv.)	NHS (equiv.)	DMBQ
Nitrogen purge[a]	9.5	–	85
Nitrogen purge[a]	8.6	2.9	81
Freeze-thaw/high vacuum[b]	5.5	–	76
Freeze-thaw/high vacuum[b]	5.3	3.2	62

[a]Prior to NO_2 reaction, the solution was twice cooled to -78°C and subjected to high vacuum for 10 min. [b]Prior to NO_2 reaction, the solution was frozen using liquid nitrogen and then melted under high vacuum; the vacuum was replaced with argon.

Concerning the reaction vessel size, there was 22% less DMBQ formed from 8 when the solvent volume was lowered from 2 to 1 mL and the headspace was simultaneously lowered from 100 to 2.5 mL. Additional headspace effects can be seen in the data given in Table 1. This yield reduction observation suggested that the amount of air in the reaction was a significant factor in NO_2 reactions. Consequently, a set of oxidations were run in the absence of air.

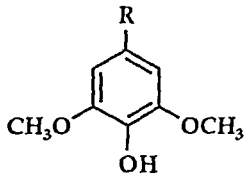
We examined two methods for air removal and two levels of NHS; the results are given in Table 4. The small variation in the absolute yields have no obvious explanation; however, it is apparent that the oxidation proceeds to a high level in the absence of air. In the two cases studied, NHS did not help the yield.

Finally, it should be noted that fresh NO_2 or material from a carefully sealed bottle should be used. We have observed poorer yields with certain batches of older NO_2.[7]

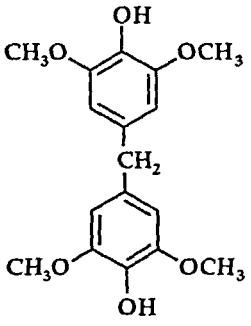
NO_2 Oxidations of Syringyl Lignin Models

Several additional model compounds have been subjected to the NO_2 oxidation conditions (Table 5). The data clearly indicate that a variety of

side chains can be oxidatively cleaved when reacting syringyl substrates with NO_2. The yields of DMBQ are high for benzyl alcohol (8), aldehyde (9), and benzyl (16) side chains, moderate for allyl (13), methyl (12), and methoxymethyl (10), and poor for a ketone (11), acid (14), and ester (15).



8, R = CH_2OH
9, R = CHO
10, R = CH_2OCH_3
11, R = $C(=O)CH_3$
12, R = CH_3
13, R = $CH_2CH=CH_2$
14, R = CO_2H
15, R = CO_2CH_3



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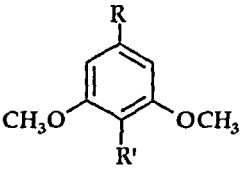


17, R = CH_2OH, R' = H
18, R = $CHCH_3$, R' = OCH_3
OH

Table 5. Yields of DMBQ from the NO_2 (5.5 equiv.) oxidations of selected syringyl models in methanol for 3 hr with 2 equiv. of NHS.

Substrate	% DMBQ
Syringyl alcohol (8)	88
Syringaldehyde (9)	90
4-Methoxymethyl syringol (10)	40
4-Methyl syringol (12)	38
4-Allyl syringol (13)	30
Disyringyl methane (16)	85[a]
Acetosyringone (11)	20
Syringic acid (14	-
Syringic acid methyl ester (15)	-
3,5-Dimethoxybenzyl alcohol (17)	-
1-(3,4,5-Trimethoxyphenyl)ethanol (18)	-[b]

[a]A 100% yield corresponds to the production of 2 equiv. of DMBQ in this case. [b]Discussed in greater depth in paper 7 in this series; the products were 18 - 60% and 9 + 10 - 40%.[10]

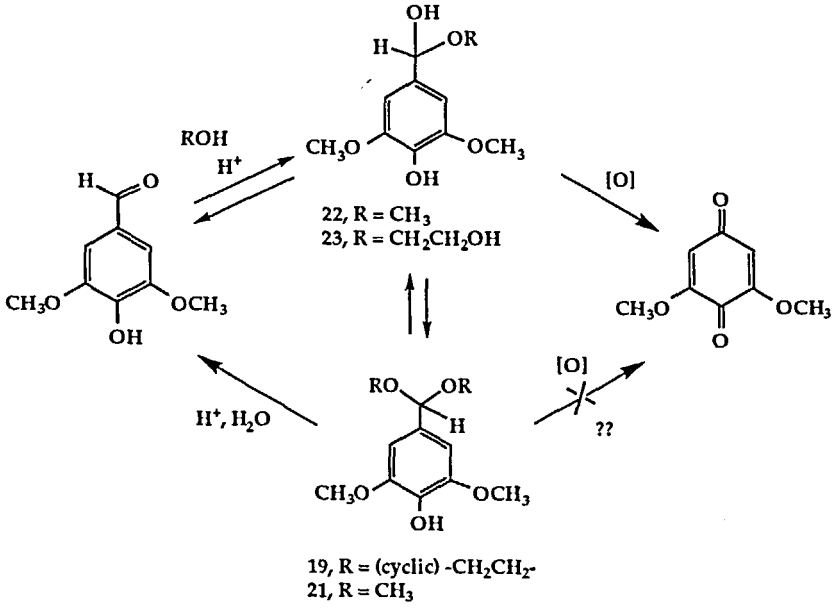


Figure 2. Proposed intermediates in the oxidation of syringaldehyde.

A phenolic hydroxyl group is essential for oxidation to a quinone; nonphenolic compounds **17** and **18** gave no quinones. Except for -CHO, carbonyl compounds generally provided poor yields of DMBQ. The oxidation of disyringyl methane, which has two syringyl units, provided nearly two equivalents of DMBQ (Table 5, entry 6). Disyringyl methane must have undergone side chain cleavage to give a highly reactive co-product, such as **8** or **9**, that was also oxidized to DMBQ.

The surprising difference in DMBQ yields from aldehyde and ketone substrates prompted us examine the possible involvement of hemiacetal and acetals in these oxidations. Hemiacetal/acetal can form between alcohol solvents and carbonyl groups in the presence of acid (Figure 2). The acid catalyst could be nitric acid (HNO_3), a disproportionation product of nitrous acid (HNO_2),[11] which is generated *in situ* by hydrogen atom extraction reactions of NO_2 with phenols. The methanol hemiacetal and acetal intermediates of syringaldehyde are not very stable;[10] therefore, we

decided to examine the NO_2/NHS oxidations in ethylene glycol, the second best pure solvent tested in the oxidation of syringyl alcohol. This solvent may also provide stable cyclic acetal products.

The reaction of syringyl alcohol with NO_2/NHS in ethylene glycol was rapid, the starting material was consumed after 10-15 min, but the DMBQ yield was only moderate (Table 1, 33%). The reaction was much slower with syringaldehyde (several hours). Again, DMBQ was observed, but the product mixture contained a substantial amount of syringaldehyde cyclic acetal (**19**). The structure of the latter was confirmed by a comparison of its GC retention time and GC/MS to that obtained from the reaction of syringaldehyde and ethylene glycol in the presence of nitric acid. Unfortunately, the acetal could not be isolated without decomposition.

Oxidation of a 2/3 mixture of syringaldehyde and syringaldehyde cyclic acetal (as determined by GC) with NO_2 in *ethylene glycol* gave only a 7% DMBQ yield. Oxidation of the same mixture with NO_2 in *methanol* gave a 61% yield of DMBQ. It appears that, over the 2-hour reaction period, approximately half of the cyclic acetal was converted (via acid catalyzed solvolysis) to a hemiacetal that was oxidized.

The NO_2/NHS oxidation of another aldehyde, vanillin (**20**), in ethylene glycol gave similar results: a 19% yield of MMBQ (**1**) after 90 min, along with a substantial amount of another component. This other component disappeared when the reaction mixture was contacted with water and vanillin was formed. Obviously, an acid catalyzed reaction had occurred between vanillin and ethylene glycol that gave a cyclic acetal, which then reverted back to vanillin upon contact with water.

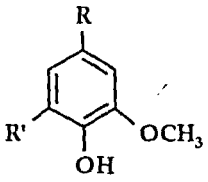
These observations lead us to conclude that aldehyde substrates, particularly syringaldehyde, may be reacting by way of their hemiacetals when NO_2 oxidations are done in methanol. In this solvent, there is probably reasonable amounts of hemiacetal **21** in equilibrium with its acetal intermediate **22**. The aldehyde-methanol hemiacetal **21** is a "benzyl alcohol," which is a reactive group towards NO_2. In contrast, in the case of ethylene glycol solvent, the cyclic acetal **19** will dominate the equilibrium between it and the acyclic hemiacetal **23**;[12] little "benzyl alcohol" will be available for conversion to DMBQ and yields will be (and are) low.

Additional oxidation studies of acetosyringone (**11**) indicated a yield of 18% DMBQ after 2 hours; only 8% of the starting material remained. Other products were not detected by GC, which implies an oxidative degradation of unknown origin. A few drops of concentrated sulfuric acid were added in one experiment to promote the formation of a hemiacetal. The yield of DMBQ did not improve. Extending the reaction time to 24 hours only improved the yield to 25%. The ketone may be slow to react because, unlike aldehydes, hemiacetal/acetal formation is rather slow.[13]

We suspect that α-carbonyl phenols are not readily oxidized by NO_2/NHS; possibly only their hemiacetals are reactive. By analogy, certain metal catalyzed oxygen reactions give high yields of DMBQ from syringyl alcohol, but no DMBQ from syringaldehyde.[14] The slow reaction and low yields of DMBQ observed for NO_2-oxidations of α-carbonyl compounds in ethylene glycol can be attributed to the co-production of unreactive cyclic acetals under the reaction conditions. Where hemiacetals are possible, the DMBQ yields can be very high - 90% for syringaldehyde in methanol. However, reaction times are somewhat long, namely 3-4 hours. The long times may be a consequence of the substrate having significant equilibrium amounts of unreactive aldehyde and acetals components presence during the reaction period.

NO_2 Oxidations of Guaiacyl Lignin Models

Unlike the simple reaction mixtures obtained from syringyl compounds, complex reaction mixtures were obtained from the NO_2 oxidation of guaiacyl models. The yields of monomethoxy-benzoquinone (MMBQ, **1**) were invariable low (< 20%). The MMBQ yields for vanillyl alcohol (**24**) varied with the amount of NO_2 used in the reaction. With 6 equiv. of NO_2 in methanol, the MMBQ yield was only 5%; with 2.5 equiv., the yield was 11-18%. Vanillyl alcohol was completely consumed. With excess NO_2, the major product was 4,6-dinitroguaiacol (**25**). The other products were 5-nitrovanillyl alcohol (**26**), 5-nitrovanillin (**27**), and 4-nitroguaiacol (**28**); their yields depended on the amount of NO_2 used.



20, R = CHO, R' = H
24, R = CH_2OH, R' = H
25, R = R' = NO_2
26, R = CH_2OH, R' = NO_2
27, R = CHO, R' = NO_2
28, R = NO_2, R' = H
29, R = $C(=O)CH_3$, R' = H
30, R = CO_2H, R' = H

Reaction temperature and pH were varied in the NO_2 oxidation of vanillyl alcohol to try to improve the yields of MMBQ. Increasing the temperature increased the reaction rate but did not affect the product distribution. Under alkaline conditions, MMBQ was not detected by HPLC.

Vanillin (20) was also examined as a model substrate for NO_2 oxidation; it behaved similarly to vanillyl alcohol (Table 6). MMBQ was not produced, but vanillin was consumed at high NO_2 levels. In the presence of 4.6 equiv. of NO_2 (entry 3) 4,6-dinitroguaiacol (25) was the main product. The nitration appears to be a stepwise process, proceeding mainly through 5-nitrovanillin (27) to give 4,6-dinitroguaiacol as a final main product. The reaction of 5-nitrovanillin with 3.3 equiv. of NO_2 gives 4,6-dinitroguaiacol in 51% yield. Increasing the NO_2 level to 20 equivalents gives 4,6-dinitroguaiacol in 83% yield.

Oxidations in ethylene glycol gave equally poor yields of MMBQ. Vanillyl alcohol (24) reacted rapidly, providing some MMBQ; however, the major product was 5-nitrovanillin (27). Compounds containing an α-carbonyl group, such as vanillin (20) and the ketone acetosyringone (29), reacted much more slowly and the MMBQ yields were poor. Vanillic acid (30) gave no MMBQ under the standard conditions, but did produce some 4,6-dinitroguaiacol (25) in the presence of excess NO_2.

An additional difficulty in obtaining good yields of MMBQ is the instability of MMBQ to prolonged exposure to NO_2 oxidation conditions. A mixture of MMBQ and NO_2 showed no significant loss of MMBQ after 90 minutes, 20% loss after 3 hours, and 77% loss after 20 hours of exposure.

The NO_2 oxidation of *p*-hydroxybenzyl alcohol, a non-methylated model, led to complete consumption of the starting material and gave no *p*-benzoquinone.

Table 6. Product composition (mol % yield) after reacting vanillin with NO_2 in the absence of NHS.

Equiv. of NO_2	Solvent	MMBQ	starting material	5-nitro-vanillin	4,6-dinitro-guaiacol	4-nitro-guaiacol
1.2	methanol	0	38	14	0	7
1.3	benzene	0	33	53	0	0
4.6	methanol	0	0	20	56	4

Possible NO_2 Mechanism

Figure 3 presents a possible set of reactions for guaiacyl structures with NO_2 in the presence of air. The fact that the material balance was low when the NO_2 concentration was low (Table 2, entry 1) suggests that competing oxidation reactions may be occurring under these conditions; the product might be an unstable *o*-benzoquinone. At higher NO_2 concentrations, vanillin is nitrated in preference to oxidation. While the nitration is shown as a simple radical coupling reaction in Figure 3, there are several reports in the literature which indicate that NO_2 reacts ortho or para to the phenolic-OH and at the site of a substituent; the resulting dienone readily rearranges to a nitrophenol product.[15]

The fact that the oxidation of syringyl compounds to DMBQ by NO_2 requires the presence of a phenolic OH group suggests that the first step in the reaction is hydrogen atom abstraction by NO_2. The production of high amounts of DMBQ in the absence of either air or NHS indicates that NO_2 is the principal oxidizing agent. A mechanism that fits our observations is presented in Figure 4. While path *a* might prevail in the absence of oxygen, we can not exclude that an oxygen pathway (*b*) is also involved. The course of events proposed in both of these mechanisms (Figures 3 and 4) are similiar to those proposed for the reactions of lignin model compounds with chlorine dioxide.[16]

The stoichiometry indicated in the proposed mechanism suggests that two equivalents of NO_2 are needed for complete oxidation. Our studies (Table 2) in the case of syringyl alcohol imply that only one equivalent is

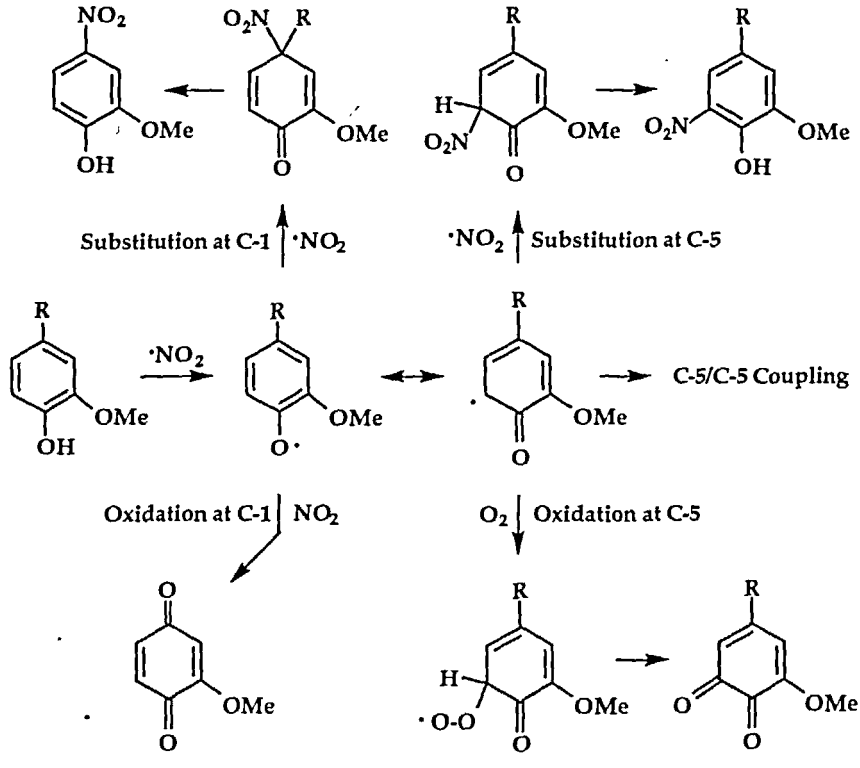


Figure 3. Reactions of NO_2 with guaiacyl structures.

necessary. However, byproducts, such as HNO_2 and NO (a radical, like NO_2), might participate in the oxidation. Nitrous acid is known to quantitatively oxidize benzyl alcohols to aldehydes; yields near 500% (based on HNO_2) have been observed in air with excess substrate.[15]

The proposed mechanism could also explain the oxidation of aldehydes, assuming that they are in equilibrium with their hemiacetal structures. The simple mechanism cannot directly account for DMBQ production from compounds having methyl, allyl, benzyl, and methyl ether side chains (**12**, **13**, **16**, and **10**). However, several of these compounds have reactive benzyl hydrogens; possibly the side chain is first oxidized to give a reactive benzylic alcohol or aldehyde group. The mixture of NO_2/NHS is capable of

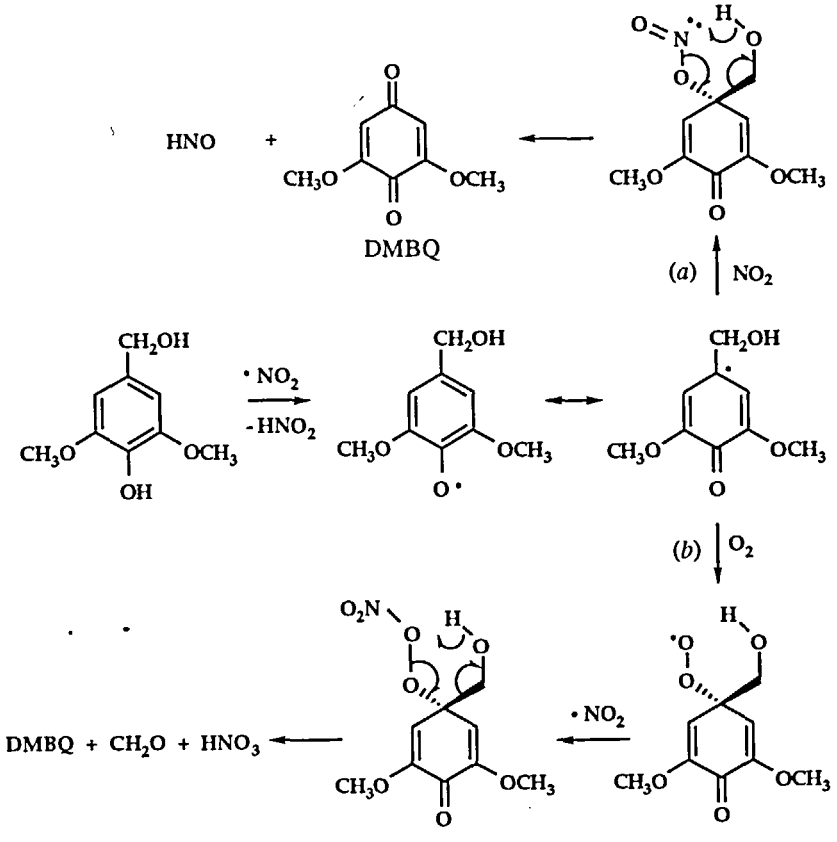


Figure 4. Proposed reaction pathways for NO_2 oxidation of a syringyl unit: (*a*) in the absence of oxygen, (*b*) in the presence of oxygen.

oxidizing benzyl alcohols to aldehydes.[10] Also, HNO_2 can oxidize benzyl alcohol or benzyl methyl ether to benzaldehyde.[15] Using this reasoning, we believe that acetals, such as **19**, are not converted to benzoquinones because benzylic oxidation would give an unreactive acid derivative.

CONCLUSIONS

Nitrogen dioxide oxidation is an excellent way to generate benzoquinones from a variety of syringyl units. Substrate reactivity appears to

depend on having a phenolic hydroxyl group and substitution at both C-3 and C-5. Guaiacyl compounds react with NO_2 to give NO_2 substitution at C-5, together with oxidation and/or replacement of side chains; the yields of MMBQ are generally low. Continued developmental work is needed to get better benzoquinone yields with guaiacyl units, since this is the predominant substructure in lignins.[5]

Oxidations performed in methanol provide the best yields. This is probably a consequence of the low solubility of DMBQ in methanol. The oxidation of syringaldehyde goes in high yield, but at a slower rate than syringyl alcohol. We believe that the aldehyde group must be in a hemiacetal form before oxidation to DMBQ can proceed. Conversion of the aldehyde to an acetal hampers reaction. Such is the case when reactions are done in ethylene glycol solvent. The oxidation is most likely radical in nature (Fig. 4). Addition of N-hydroxysuccinimide generally provides small improvements in benzoquinone yields.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Gemini 300 spectrometer and reported by chemical shifts (relative to TMS), splitting patterns (singlet, doublet, triplet, quartet, pentet, multiplet), integration areas, and proton assignments. Gas chromatographic (GC) analyses on a Hewlett-Packard 5890 GC employed a HP-17 packed column, helium carrier gas flow rate of 22 mL/min., column temperature 150°C (1 min), 10°C/min to 275°C (hold), injector temperature 250°C, and detector temperature 275°C. Mass spectrometry (MS) analyses on a Hewlett-Packard 5890 GC-MS system employed a fused silica DB-5 capillary column (30 m x 0.25 mm x 0.25 μm), column temperature 150°C (1 min), 5°C/min to 280°C (hold), injector temperature 250°C, detector temperature 280°C, helium carrier gas at 30 mL/min, a jet separator at 275°C, a source temperature of 200°C, and an ionization voltage of 70 ev. Column chromatography purifications used Merck, 230-400 mesh, Grade 60, 60Å Silica Gel. Melting points are uncorrected.

Samples of monomethoxy-[17] and 2,6-dimethoxy-*p*-benzoquinone[18] (**1** and **2**, MMBQ and DMBQ), syringic acid methyl ester (**15**),[19] and 2,6-di-

methoxy-4-(methoxymethyl)phenol (**10**)[20] were prepared by standard literature procedures; physical properties were identical to reported values. Syringyl alcohol (**8**),[21] methyl syringol (**12**),[21] disyringyl methane (**16**),[21] and 1-(3,4,5-trimethoxyphenyl)ethanol (**18**)[10] were available from other studies in our laboratory. Nitrogen dioxide, anthraquinone, N-hydroxysuccimide (**4**), succinimide (**7**), syringaldehyde (**9**), acetosyringone (**11**), 4-allyl-2,6-dimethoxyphenol (**13**), syringic acid (**14**), 3,5-dimethoxybenzyl alcohol (**17**), vanillyl alcohol (**24**), vanillin (**20**), 5-nitrovanillin (**27**), acetoguaiacone (**29**), and vanillic acid (**30**) were commercially available.

Standard NO_2 Oxidation Procedure (Syringyl Compounds). In a 100 mL two-necked round bottom flask was placed 20-30 mg of lignin model compound and 2-3 equiv. (~30 mg) of N-hydroxysuccinimide (NHS) dissolved in 2 mL of anh. methanol. A weighed amount (generally 5-6 equivalents, 20-30 mg) of liquid NO_2 in a pressure-lock gas syringe was injected into the stirred reaction mixture. The headspace displayed a white vapor that disappeared quickly; the color of the solution turned to orange-yellow. As the reaction proceeded, an orange-yellow solid, DMBQ (**2**), precipitated. The reaction mixture was allowed to stir at ambient temperature for 2 hrs; following this, 2 mL of a chloroform solution, containing 1 mg/mL anthraquinone (GC internal standard), was added. The solid DMBQ dissolved. The solution was then analyzed by GC to determine DMBQ amounts and by GC-MS to identify other reaction products. The DMBQ (**2**) was identified by direct comparison of the GC retention time and mass spectrum to an authentic sample; an ^{1}H-NMR spectrum of the precipitate was identical to authentic DMBQ. The signal response factor for DMBQ vs internal standard was 1.0/2.2.

NO_2 Oxidation Vanillyl Alcohol (24). The procedure and work-up were the same as above; however, the products did not precipitate from the reaction mixture. Product analysis by GC and GC-MS, with comparisons to authentic samples where possible, indicated the presence of MMBQ, 4-nitroguaiacol (**28**), 5-nitrovanillin (**27**), 5-nitrovanillyl alcohol (**26**), and 4,6-dinitroguaiacol (**25**). With excess NO_2, **25** was the major product; at lower levels of NO_2, 5-nitrovanillyl alcohol was the major product. 5-Nitrovanillyl alcohol was prepared by $NaBH_4$ reduction of 5-nitrovanillin (**27**) and also isolated by silica gel column chromatography

from a large scale NO_2 oxidation of vanillyl alcohol; both samples had the same spectral properties, including: ^{1}H-NMR ($CHCl_3$) δ 2.0 (s, 1, ROH), 3.97 (s, 3, OCH_3), 4.68 (s, 2, CH_2), 7.20 (d, J = 1 Hz, 1, ArH), 7.68 (d, J = 1 Hz, 1, ArH), and 10.76 (s, 1, ArOH). The yield data are given in the text. The mass spectral data for the other tentatively identified compounds were:

4,6-Dinitroguaiacol (25): *m/z* (%) 214 (M+, 100), 197 (85), 196 (26), 166 (28), 122 (26), 121 (39), 93 (20), 79 (26), 53 (29), and 50 (28).

4-Nitroguaiacol (28): *m/z* (%) 169 (M+, 100), 139 (21), 123 (22), 111 (14), 108 (25), 80 (14), 65 (16), and 52 (25).

NO_2 Oxidation Vanillin (20). The procedure and work-up were the same as above; however, the products did not precipitate from the reaction mixture. Product analysis was done by GC and GC-MS; comparisons were made to authentic samples and those from the previous experiment. The reaction produced varied amounts 5-nitrovanillin (**27**), 4,6-dinitroguaiacol (**25**), and small amounts of an acetal and hemiacetal of **27**. The yields of **27** and **25** varied with the amount of NO_2 used, as explained in the text. [The yield of **25** was based on the assumption that **27** and **25** have the same GC response factors.] Treatment of **27** with excess NO_2 in methanol gave **25**.

NO_2 Oxidation Syringaldehyde (9) in Ethylene Glycol. The procedure and workup were the same as above except that the solvent was ethylene glycol. The GC analysis displayed a long time retention signal at 13.9 min which was assigned to the cyclic acetal (**19**). The latter was identical in retention time and mass spectrum to a sample of **19** prepared by mixing syringaldehyde in ethylene glycol with a catalytic amount of *p*-toluenesulfonic acid. Compound **19** was very unstable and decomposed upon various attempted isolations. A mixture of 3 parts acetal and 2 parts syringaldehyde was the highest ratio of acetal that was possible. The mass spectrum of cyclic acetal (**19**) was as follows: *m/z* (%) 226 (56, M^+), 225 (51), 181 (43), 167 (21), 154 (48), and 73 (100).

Nitrogen Dioxide Oxidation under Oxygen-Free Conditions. A solution of syringyl alcohol (20 mg, 0.11 mmol) in 5 mL of anhyd. methanol in a two-neck flask was frozen by immersion into a cooling bath containing liquid nitrogen. The solid mixture was then evacuated (0.03 mm Hg) and allowed to melt under vacuum. The vacuum was then re-

placed with argon. When the reaction flask had warmed to room temperature both necks were closed. To the stirred reaction mixture was added a weighed amount of nitrogen dioxide (5-6 equivalents) using a gas-tight syringe. Fumes were produced; however, these disappeared in a few minutes. The color of the solution turned orange and a pale yellow precipitate slowly formed. After stirring at room temperature for 2 hours, the reaction flask was evacuated using a water aspirator. Both necks were then open to the atmosphere and enough chloroform was added to dissolve all of the precipitate. Analysis of a sample for DMBQ was done by GC, using anthraquinone as an internal standard. The above experiment was also conducted with the addition of N-hydroxysuccinimide (44 mg, 0.308 mmol, 3.3 equivalents) before freezing. In addition, the oxygen-free conditions with syringyl alcohol were conducted by preparing a solution of syringyl alcohol in anhyd. methanol, and repetitively cooling to -78°C under high vacuum for 10 min, and then releasing nitrogen into the container. Nitrogen dioxide was added with a gas-tight syringe and reaction allowed to stir under a nitrogen atmosphere. A similar experiment was done in the presence of NHS. Yield data for each of these experiments are given in the text.

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