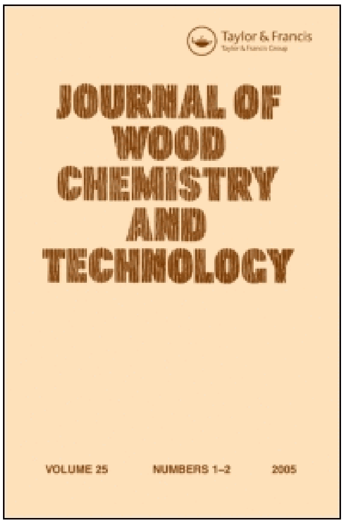


## Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# Reactions of Metal Ion Complexes with Lignin Model Compounds, Part II. Fe(TSPC) Catalyzed Formation of Oxidized Products in the Absence of Oxygen

Paul A. Watson[a]; L. James Wright[a]; Terry J. Fullerton[b]
[a] Department of Chemistry, University of Auckland, Auckland, New Zealand [b] Pulp and Paper Research Organization of New Zealand Forest Research Institute, Rotorua, New Zealand

**To cite this Article** Watson, Paul A. , Wright, L. James and Fullerton, Terry J.(1993) 'Reactions of Metal Ion Complexes with Lignin Model Compounds, Part II. Fe(TSPC) Catalyzed Formation of Oxidized Products in the Absence of Oxygen', Journal of Wood Chemistry and Technology, 13: 3, 391 — 409

**To link to this Article: DOI:** 10.1080/02773819308020524

**URL:** http://dx.doi.org/10.1080/02773819308020524

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 13(3), 391-409 (1993)

# REACTIONS OF METAL ION COMPLEXES WITH LIGNIN MODEL COMPOUNDS, PART II. Fe(TSPC) CATALYZED FORMATION OF OXIDIZED PRODUCTS IN THE ABSENCE OF OXYGEN.

Paul A. Watson and L. James Wright*
Department of Chemistry
University of Auckland
Private Bag 92019
Auckland, New Zealand

Terry J. Fullerton
Pulp and Paper Research Organization of New Zealand
Forest Research Institute
Private Bag 3020
Rotorua, New Zealand

## ABSTRACT

The water soluble phthalocyanine complex trisodium tetra-4-sulfonatophthalocyanineiron(III) (Fe(TSPc)) was found to be an effective catalyst for the cleavage of the β-ether bonds in the phenolic lignin model compounds guaiacylglycol β-guaiacyl ether (**1**) and guaiacylglycerol β-guaiacyl ether (**11**). The products of these reactions were very different from those formed in the corresponding reactions catalyzed by anthraquinone (AQ) or Co(TSPP).[1-4] In particular, they gave large quantities of oxidized products, even though the reactions were performed in the absence of oxygen or other added oxidant. Mechanisms have been proposed for the oxidation reactions involving **1** and **11**. In both cases the first step involves one electron oxidation of the lignin model compound by the catalyst. The radical derived from **1** then undergoes further one electron oxidation and deprotonation to give 4'-hydroxy-3'-methoxy-1-(2"-methoxyphenoxy)acetophenone (**8**) whereas that derived from **11** undergoes Cα-Cβ bond cleavage to give vanillin (**4**). Reactions of the reduced form of the catalyst with **8** and the quinone methides produced from the phenolic models are important routes for guaiacol formation and regeneration of the oxidized form of the catalyst. The feasibility of these proposed reaction pathways was investigated by studying the reactions of the intermediate compounds with the catalyst.

## INTRODUCTION

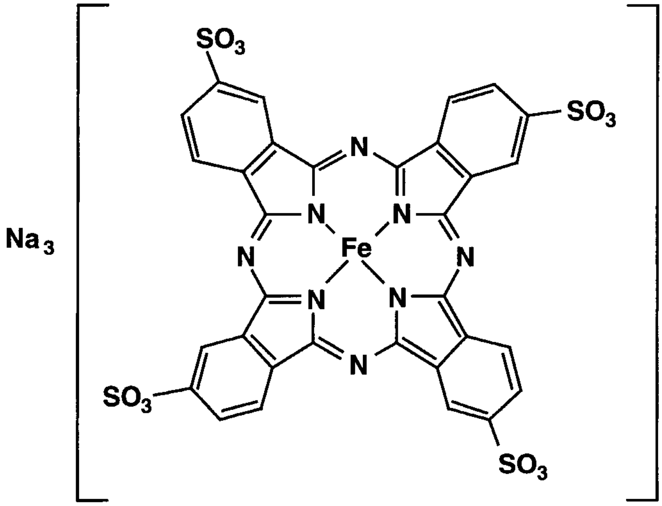
We have previously reported that the water soluble trisodium tetra-4-sulphonatophthalocyanineiron, (Fe(TSPc)), is an active catalyst for the cleavage of the β-aryl ether bond in the lignin model compound **1**.[2-4] In addition, large amounts of oxidized products were formed, even in the presence of added glucose. This is significant, as selective oxidation of lignin to form α-carbonyl groups is known to dramatically enhance the rate of lignin degradation under kraft pulping conditions.[5] The oxidation of lignin model compounds by metalloporphyrins, in conjunction with added oxidizing agents, has been well documented by others in systems that have been designed to mimic lignin degrading enzymes such as those found in white rot fungi.[6-9] However, the oxidized products formed by Fe(TSPc) in the model compound reactions described here were formed in the absence of oxygen or other added oxidant. Our preliminary results relating to the mechanisms of these reactions and also those involving β-aryl ether bond cleavage are described in this paper.

## RESULTS AND DISCUSSION

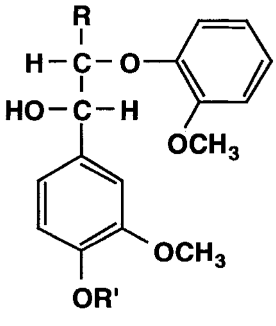
### Reactions Of The β-Ether Lignin Model Compound 1

The model reactions were carried out in sealed glass tubes at 135°C under a nitrogen atmosphere as described in Part I of this series.[1] The results are therefore directly comparable.

The product distributions for both the Fe(TSPc) and Fe(TSPc)/glucose catalyzed reactions of **1** are given in Table 1. The results obtained for the AQ catalyzed reactions are also given for comparison. Based on the amounts of guaiacol (**2**) formed, it can be seen that in the presence of glucose Fe(TSPc) was slightly more active than AQ. However, in contrast to AQ, this catalyst still produced considerable quantities of guaiacol (**2**) when glucose was absent. Similar amounts of vinyl guaiacol (**3**) were produced by both catalysts, but there was considerable variation in the other products formed. In particular, the α-carbonyl compounds **5** and **8** were very prominent in the Fe(TSPc) catalyzed reactions, especially when glucose was absent.



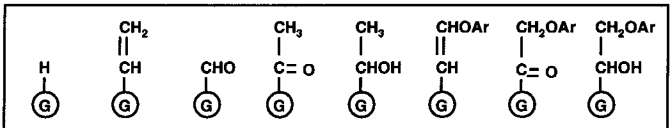
**Trisodium tetra-4-sulfonatophthalocyanineiron(III) (Fe(TSPc))**



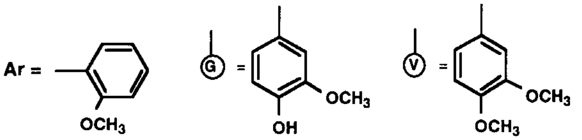
| | |
|---|---|
| R=H, R'=H; | guaiacylglycol β-guaiacyl ether (1) |
| R=H, R'=$CH_3$; | veratrylglycol β-guaiacyl ether (10) |
| R=$CH_2OH$, R'=H; | guaiacylglycerol β-guaiacyl ether (11) |

FIGURE 1. The Catalyst Fe(TSPc) and Lignin Model Compounds **1**, **10** and **11**

TABLE 1. Total Reaction Component Analysis for **1**[a]



| Catalyst | %**2** | %**3** | %**4** | %**5** | %**6** | %**7** | %**8** | %**1** |
|---|---|---|---|---|---|---|---|---|
| Control | 23 | | 3 | | | 37 | | 40 |
| Control/Gl | 33 | 4 | | | 1 | 29 | | 32 |
| AQ | 30 | 9 | 4 | 1 | 2 | 16 | | 10 |
| AQ/Gl | 65 | 18 | 1 | 2 | 5 | 2 | | 17 |
| Fe(TSPc) | 63 | 7 | | 41 | 3 | | 26 | |
| Fe(TSPc)/Gl | 71 | 12 | | 20 | | | 11 | |

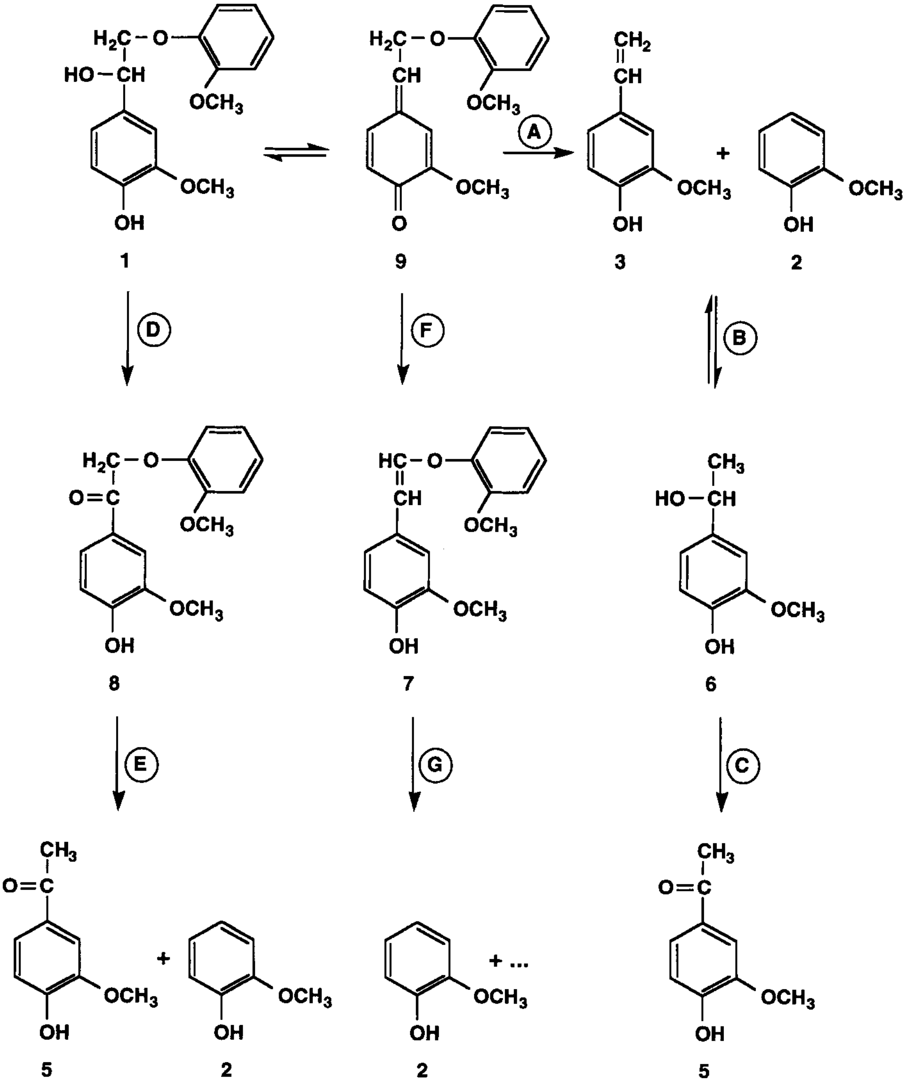


**Gl** = glucose, **AQ** = anthraquinone

[a] Conditions: 135°C, $N_2$, 1 M NaOH, 2hr; control = 1 M NaOH solution alone; mole ratios, compound : catalyst : glucose = 1 : 0.1 : 2.15

The products of the Fe(TSPc) catalyzed reactions of **1** can be rationalized in terms of the reaction pathways depicted in Scheme 1. The feasibility of each pathway was investigated by studying the reactions of the proposed intermediates with the Fe(TSPc) catalyst.

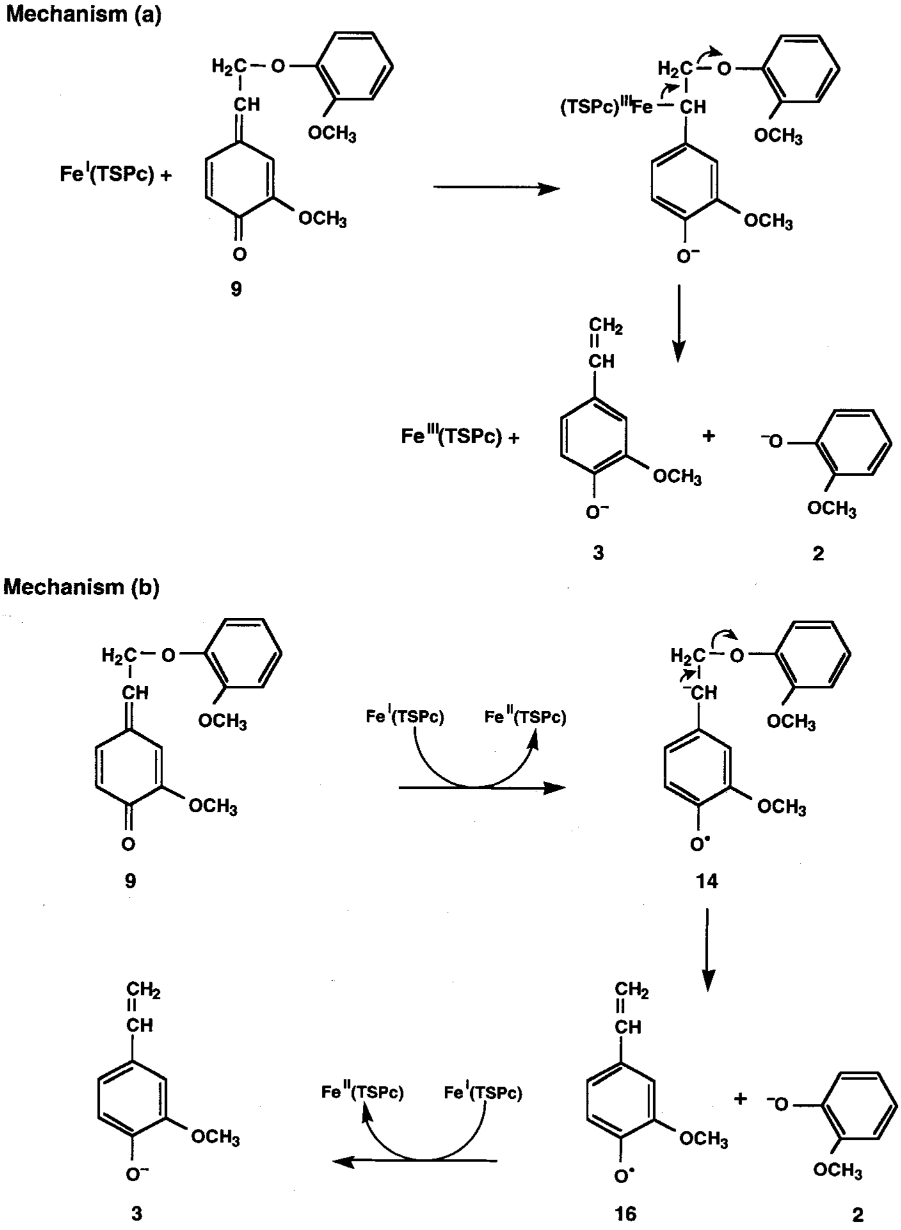
In aqueous solution and in the absence of air, there are three stable, formal oxidation states available for the iron atom in Fe(TSPc) i.e. $Fe^{I}$, $Fe^{II}$, and $Fe^{III}$.[10] The iron phthalocyanine catalyst was always added at the beginning of each reaction as the air stable, deep blue $Fe^{III}$(TSPc) form. It was found that on heating this material under nitrogen with glucose in 1M sodium hydroxide solution, complete and rapid conversion to the red $Fe^{I}$(TSPc) occurred. This change could be conveniently monitored by UV-vis spectroscopy.[10]



SCHEME 1. Rationalization of Product Distribution Obtained from Reaction of **1** with Fe(TSPc)

Reduction to $Fe^{I}$(TSPc) in aqueous 1 M sodium hydroxide solution could also be achieved by stirring $Fe^{III}$(TSPc) with zinc amalgam at room temperature. In an experiment to test the feasibility of pathway A in Scheme 1, aqueous $Fe^{I}$(TSPc) was generated this way and then stirred with a dichloromethane solution containing a stoichiometric quantity of the quinone methide **9**. The experimental conditions used were the same as those described for the reaction of **9** with $Co^{II}$(TSPP) in Part I of this series.[1] The reaction was allowed to continue for one hour at room temperature in the dark. Isolation and analysis of the organic fraction revealed that guaiacol (**2**) (27%) and vinyl guaiacol (**3**) (7%) were both produced. In control experiments, reaction of the quinone methide **9** with zinc amalgam alone gave **2** (2%) and the vinyl ether **7** (1%) while reaction with $Fe^{III}$(TSPc) alone gave **2** (2%) and **7** (5%). Thus reaction of the reduced catalyst $Fe^{I}$(TSPc) with quinone methide **9** (pathway A) is a plausible route for guaiacol (**2**) and vinyl guaiacol (**3**) formation.

Less can be said with certainty about the mechanism of this reaction compared to that catalyzed by Co(TSPP) since +1, +2, and +3 are all well defined oxidation states for iron in this system. Thus, mechanisms involving single electron transfer or adduct formation followed by breakdown involving overall transfer of two electrons are both possibilities which should be considered. In mechanism (a) Scheme 2, initial reaction of $Fe^{I}$(TSPc) with quinone methide **9** gives a substituted alkyl complex which then undergoes heterolytic cleavage of the Fe-C bond with overall transfer of two electrons from the iron complex in a manner analogous to the "adduct mechanism" that has been proposed in the past for the reaction of AHQ with **9**.[11,12] However, the intermediate shown in Scheme 2 would be very sterically crowded. If it does form, it must be very unstable as considerable amounts of guaiacol and vinyl guaiacol were formed at 20°C in the reaction of $Fe^{I}$(TSPc) with the quinone methide **9**. The single electron transfer mechanism shown in (b) Scheme 2 is essentially the same as that already proposed for Co(TSPP).[1] Cleavage of the β-aryl ether bond occurs after transfer of an electron to the quinone methide **9**.[13,14] By analogy with the Co(TSPP) catalyzed reactions and in the absence of evidence to the contrary, this is the favoured mechanism here.



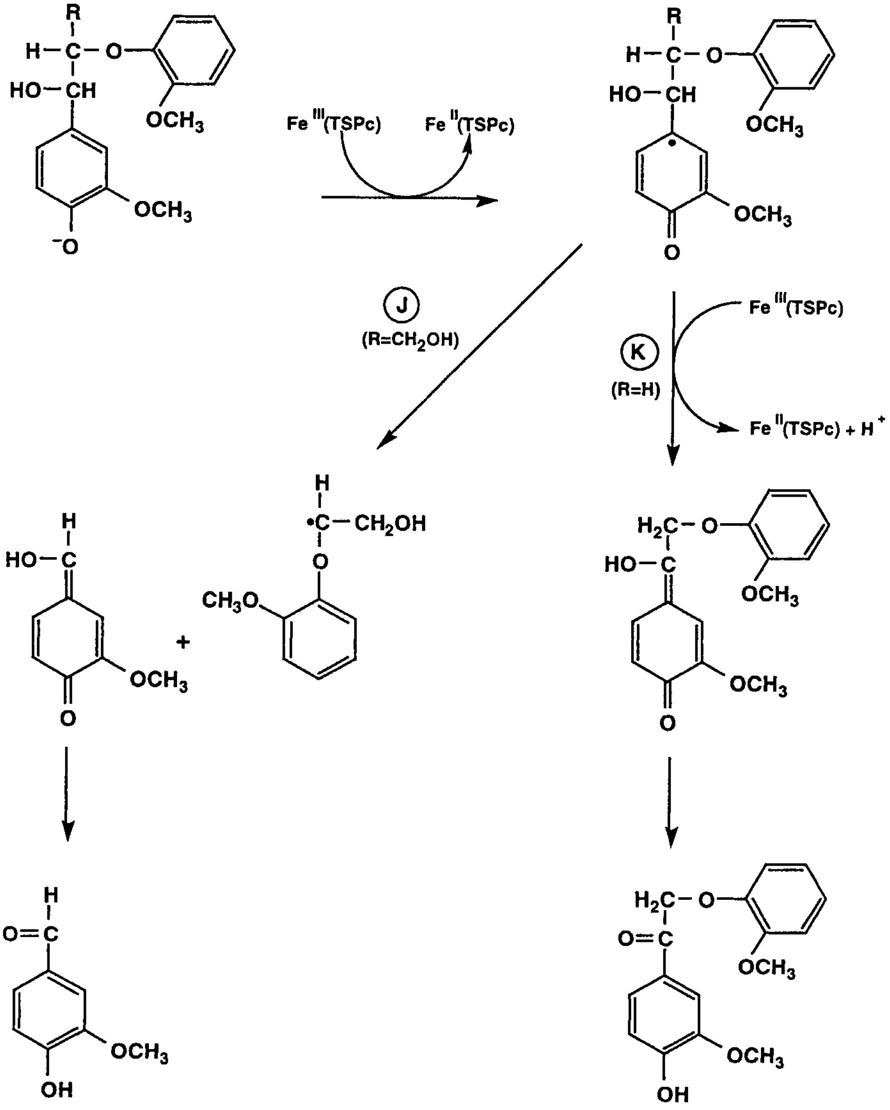
SCHEME 2. Possible Mechanisms for Reaction of Fe$^I$(TSPc) with Quinone Methide **9**

## Formation Of α-Carbonyl Compounds From 1

A major difference between the Fe(TSPc) catalyzed reactions of **1** compared to those catalyzed by AQ or Co(TSPP) is the formation of considerable quantities of the oxidized compounds **8** and **5**. Significantly larger amounts were formed in the absence of glucose (Table 1). The most likely source of the α-carbonyl compound **8** is via oxidation of **1** by an oxidized form of the catalyst, i.e. $Fe^{III}$(TSPc) or $Fe^{II}$(TSPc), with concomitant reduction of the catalyst ultimately giving $Fe^{I}$(TSPc). In support of this, formation of the red $Fe^{I}$(TSPc) was still observed to occur in the reactions of **1** to which no reducing glucose had been added. The formation of some **8** in the Fe(TSPc)/glucose catalyzed reaction indicates that **1** must compete with glucose to some extent as reductant for the oxidized catalyst.

A possible mechanism for the formation of the α-carbonyl compound **8** is depicted in Scheme 3. The key step involves single electron transfer from **1** to an oxidized form of the catalyst. Single electron transfer mechanisms have been demonstrated for the oxidation of related compounds using oxidants such as cobalt(III) acetate, Mn(II)/$O_2$, or $S_2O_8^{2-}/Cu^{2+}$.[15,16] Cleavage of the Cα-Cβ bond or further oxidation to α-carbonyl products then follows the initial electron transfer step. The particular pathway depends on the nature of the compound and in particular the substituents on the phenyl rings. The absence of vanillin (**4**) in the products of the Fe(TSPc) catalyzed reactions of **1** indicates that oxidation to the α-carbonyl compound **8** (pathway K) is preferred to Cα-Cβ bond cleavage (pathway J) in this case. (Note that pathway J is favoured for the phenylpropane model **11** - see below).

An alternative mechanism involving β-hydride elimination from a coordinated alkoxide (derived via deprotonation of the α-hydroxy group of **1** after coordination to Fe(TSPc)) is unlikely since there would be no vacant cis coordination sites in a complex such as this.[17]

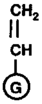
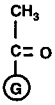
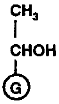
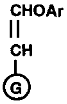
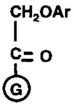
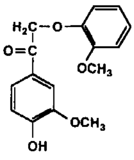
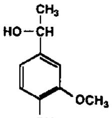
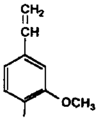
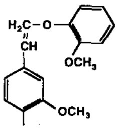


4

8

SCHEME 3. Proposed mechanisms for the formation of the oxidized products **8** and **4** from the model compounds **1** and **11** respectively

TABLE 2. Products from Proposed Intermediate Compounds[a]

| | |  $H{-}$Ⓖ |  $CH_2{=}CH{-}$Ⓖ |  $CHO{-}$Ⓖ |  $CH_3{-}C{=}O{-}$Ⓖ |  $CH_3{-}CHOH{-}$Ⓖ |  $CHOAr{=}CH{-}$Ⓖ |  $CH_2OAr{-}C{=}O{-}$Ⓖ |
|---|---|---|---|---|---|---|---|---|
| | Catalyst | %2 | %3 | %4 | %5 | %6 | %7 | %8 |
|  8 | Control | 9 | | | | | | 89 |
| | Control/Gl | 11 | | | 5 | | | 87 |
| | Fe(TSPc) | 19 | | | 6 | | | 74 |
| | Fe(TSPc)/Gl | 34 | | | 31 | | | 53 |
|  6 | Control | | 29 | | | 10 | | |
| | Control/Gl | | 24 | | | 12 | | |
| | Fe(TSPc) | | 22 | | 24 | | | |
| | Fe(TSPc)/Gl | | 17 | | 5 | | | |
| | Fe(TSPc)(100%) | | 1 | 3 | 63 | 1 | | |
| | Fe(TSPc)(100%)/Gl | | 6 | 3 | 26 | 3 | | |
|  3 | Control | | 22 | | | 12 | | |
| | Control/Gl | | 23 | | 10 | | | |
| | Fe(TSPc) | | 16 | | | 12 | | |
| | Fe(TSPc)/Gl | | 13 | | | 8 | | |
| | Fe(TSPc)(100%) | | | 3 | 18 | | | |
| | Fe(TSPc)(100%)/Gl | | 3 | 3 | 5 | 3 | | |
|  7 | Control | 9 | | | | | 65 | |
| | Control/Gl | 7 | | | | | 31 | |
| | Fe(TSPc) | 37 | | | 2 | | 31 | |
| | Fe(TSPc)/Gl | 30 | | | | | 35 | |

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

## Reactions Of Proposed Intermediate Compounds

The possibility that the α-carbonyl compound **8** might be slowly degraded during the catalytic reactions of **1** and thereby act as a precursor to other products was investigated by studying its reactions under catalytic conditions. Reaction of the α-carbonyl compound **8** with Fe(TSPc) alone yielded unreacted starting material **1** (74%) and only slightly increased quantities of guaiacol (**2**) compared to the controls (Table 2). However, increased reactivity was observed with Fe(TSPc)/glucose where guaiacol (**2**) (34%), acetovanillone (**5**) (31%) and unreacted **8** (53%) were isolated. This indicates the reduced catalyst, $Fe^{I}$(TSPc), converts **8** into **2** and **5** in a slow, but relatively clean reaction. Compounds **2** and **5** are formed in almost equivalent amounts from the reaction of Fe(TSPc)/glucose with **8**. It is therefore reasonable to assume that the amount of **5** formed in the reaction of **1** with Fe(TSPc)/glucose (20%, Table 1) indicates the upper limit to the amount of guaiacol that is formed via pathway E, Scheme 1. On the basis of this assumption, and the observation that only a small amount of compound **8** (11%) was produced in the reaction of **1** with Fe(TSPc)/glucose, it appears that pathways D and E (Scheme 1) are not the major reaction paths in this case. Reaction of **1** with Fe(TSPc) in the absence of glucose gives much greater amounts of **5** and **8** (Table 1). Therefore, pathways D and E (Scheme 1) may well be major reaction paths for **1** in this case. The reduced catalyst, $Fe^{I}$(TSPc), is formed during the conversion of **1** to **8** via pathway D and is then available to react with **8** to produce **5** and **2** via pathway E. A possible mechanism for pathway E is discussed in Part III of this series.[18]

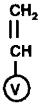
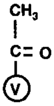
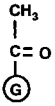
Reaction of **1** via pathway A in Scheme 1 leads to both vinyl guaiacol (**3**) and guaiacol (**2**), although relatively little of this former compound was isolated (Table 1). Vinyl guaiacol (**3**) is reactive under the conditions employed and the products formed on its reaction with Fe(TSPc) are presented in Table 2. A small amount of apocynol **6** was formed in reactions with Fe(TSPc) (10%), both with and without glucose; no other products were detected. By analogy with the observed oxidation of **1** to **8**, some oxidation of apocynol (**6**) to acetovanillone (**5**) might have been expected, especially in the reaction with no added glucose. However, this oxidation reaction here could not have occurred catalytically as there was no oxidant available to reoxidize the $Fe^{I}$(TSPc) once it formed. In contrast, for reactions involving **1** the reduced catalyst could be reoxidized through reaction with the quinone methide **9**. Thus it was found that on reaction of vinyl guaiacol (**3**) with an equimolar quantity of $Fe^{III}$(TSPc), acetovanillone (**5**) (18%) was formed when glucose was absent. Only a small amount of acetovanillone (**5**) (5%) was formed in a corresponding reaction in the presence of glucose. Thus pathways B and C in Scheme 1 provide another route to the oxidized product acetovanillone (**5**) in the Fe(TSPc) catalyzed reactions of **1**.

Reactions with apocynol (**6**) showed similar trends with more acetovanillone (**5**) formed in the absence of glucose (24%) (Table 2). With an equimolar quantity of $Fe^{III}$(TSPc) and no glucose added, large amounts of **5** (63%) were formed. The mechanism for the formation of **5** from **6** is probably similar to that for the formation of **8** from **1** (pathway K, Scheme 3).

Significant amounts of guaiacol (**2**) were formed in the Fe(TSPc) catalyzed reactions of the vinyl ether **7** (Table 2), in contrast to the Co(TSPP) catalyzed reaction.[1] The yield was similar with and without glucose, indicating that there may be more than one mechanism for guaiacol (**2**) formation from **7**. The absence of any vinyl ether **7** in the products of the reactions of Fe(TSPc) with **1** indicates pathway F in Scheme 1 does not successfully compete with paths A and D.

To summarize, we propose that pathway A (Scheme 1) is the major route to guaiacol (**2**) formation in the presence of added glucose. The oxidized α–carbonyl compounds **8** and **5** are formed via pathways D, E and C, although these routes are of reduced importance in this case since the added glucose competes with **1** and **6** as a reductant for the oxidized catalyst, $Fe^{III}$(TSPc). When no glucose is added, D and C become very important and provide a means of generating the reduced catalyst $Fe^{I}$(TSPc). The reduced catalyst is then available to react with the α-carbonyl compound **8** and the quinone methide **9** (via pathways E and A respectively) to produce guaiacol (**2**).

TABLE 3. Products from the Non-phenolic Model Compound **10**[a]

| |  |  |  |  |
|---|---|---|---|---|
| Catalyst | %**2** | %**27** | %**29** | %**5** |
| Control | 3 | | | |
| Control/Gl | 10 | | | |
| AQ/Gl | 17 | 3 | | |
| Fe(TSPc) | 26 | | 6 | 7 |
| Fe(TSPc)/Gl | 22 | | 4 | 5 |

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

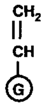
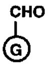
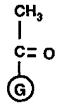
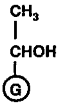
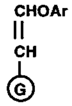
## Reactions With Non-phenolic β-Ether **10**

The products formed on reaction of the non-phenolic β-ether **10** are presented in Table 3. Although relatively small amounts of guaiacol (**2**) were formed, considerably more was produced than in the control reactions and those catalyzed by AQ. The other products formed were completely different to those found in the AQ and Co(TSPP) catalyzed reactions of **10**.[1] The α-carbonyl compound **29** is probably formed via reactions analogous to those in pathways D and E of Scheme 1. The presence of small quantities of acetovanillone (**5**) means that the iron catalyst has some capacity to demethylate aryl methyl ethers. This potentially important reaction is discussed in more detail in Part III of this series.[18] As expected, slightly more of these two oxidized products was formed in the absence of added glucose.

## Reactions With The Phenylpropane Lignin Model Compound **11**

Reactions with the phenylpropane model compound **11** were also investigated and the results are given in Table 4. Larger amounts of guaiacol (**2**)

TABLE 4. Total Reaction Component Analysis for **11**[a]

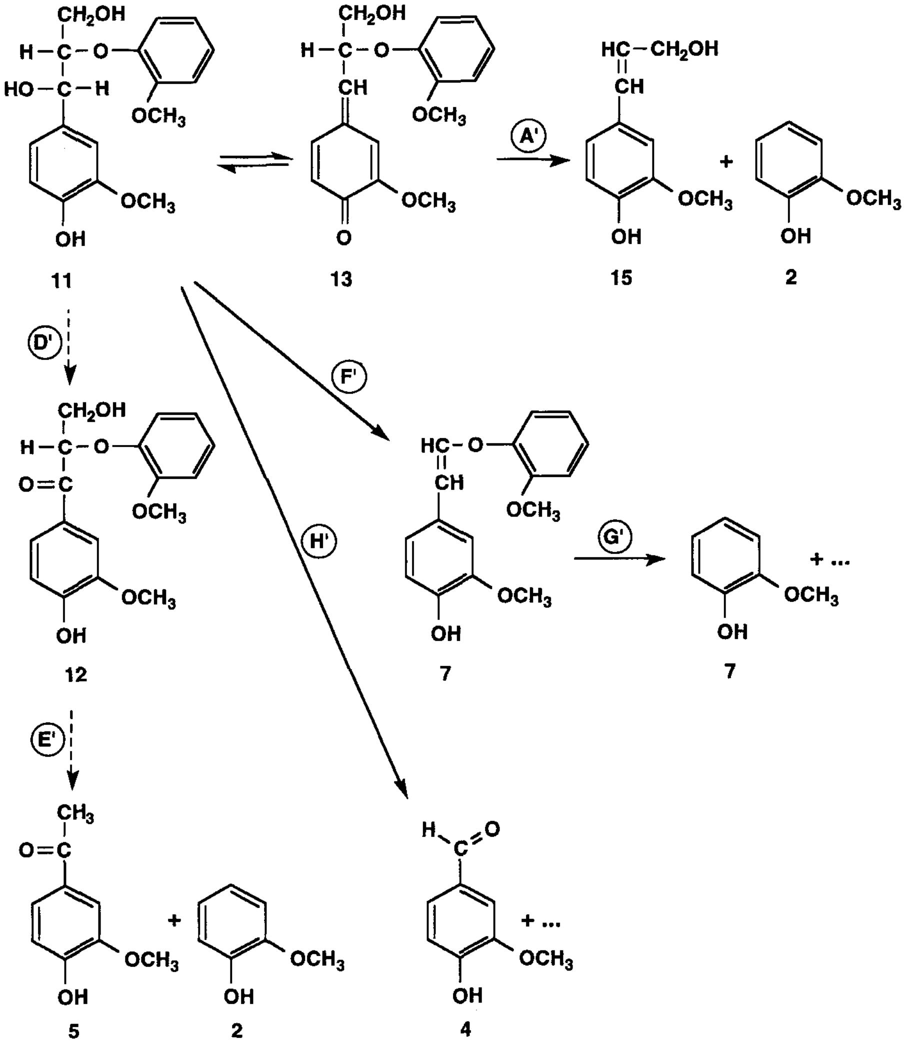
| |  $\mathrm{G{-}H}$ |  $\mathrm{G{-}CH{=}CH_2}$ |  $\mathrm{G{-}CHO}$ |  $\mathrm{G{-}C({=}O){-}CH_3}$ |  $\mathrm{G{-}CHOH{-}CH_3}$ |  $\mathrm{G{-}CH{=}CHOAr}$ |
|---|---|---|---|---|---|---|
| Catalyst | %**2** | %**3** | %**4** | %**5** | %**6** | %**7** |
| Control | 16 | | 5 | | | 56 |
| Control/Gl | 15 | | 2 | | | 50 |
| AQ/Gl | 43 | 2 | 6 | | 1 | 22 |
| Fe(TSPc) | 59 | 2 | 21 | 5 | 1 | 8 |
| Fe(TSPc)/Gl | 63 | 2 | 20 | 5 | 1 | |

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

were formed in the Fe(TSPc) catalyzed reactions than in the controls. The product distributions were different to those obtained when either AQ or Co(TSPP) was the catalyst.[1] A significant quantity of vanillin (**4**) was formed along with a small amount of acetovanillone (**5**). In addition, very little vinyl ether **7** was isolated.

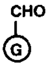
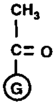
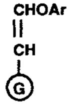
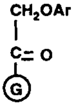
Formation of these products can be rationalized in terms of the reaction pathways in Scheme 4. The quinone methide **13** is expected to be a reasonable route to guaiacol (**2**) (via pathway A') by analogy to the reactions of **1**. In the absence of glucose, the reduced form of the catalyst (which is necessary for reaction with the quinone methide **13**) could be produced by reaction with **11** or products derived from **11**. Coniferyl alcohol (**15**) was not detected as one of the products, probably because it is reactive under the conditions used.[19]

An important pathway for the reaction of model compound **1** with Fe(TSPc) involves oxidation to the α-carbonyl compound **8**. However, the analogous reaction to give the α–carbonyl compound **12** from **11** (pathway D') does not



SCHEME 4. Rationalization of product distribution obtained from reaction of **11** with Fe(TSPc)

TABLE 5. Products from **12**[a]

| |  |  |  |  |  |
|---|---|---|---|---|---|
| Catalyst | %**2** | %**4** | %**5** | %**7** | %**8** |
| Control | 16 | 3 | 1 | 5 | 10 |
| Control/Gl | 21 | 2 | 3 | 2 | 24 |
| AQ/Gl | 22 | 2 | 4 | | 30 |
| Fe(TSPc) | 17 | 4 | 6 | | 21 |
| Fe(TSPc)/Gl | 25 | 2 | 12 | | 33 |

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

appear to occur to any great extent. This can be deduced from the observation that significant amounts of the phenylethane α-carbonyl compound **8** was formed in the reaction of the phenylpropane α-carbonyl compound **12** with Fe(TSPc) (Table 5) and yet **8** was completely absent from the reaction products of **11**. In addition, no **12** was observed by $^{13}$C NMR analysis in this latter reaction (Table 4). Thus pathways D' and E' are of limited importance here.

In contrast to the reactions of **1**, considerable amounts of vanillin (**4**) were formed from **11**. The absence of the α-carbonyl compound **12** (or its expected degradation product **8**) and the presence of vanillin (**4**) can both be explained if the oxidation reaction proceeds via mechanism J in Scheme 3. Here, homolytic cleavage of the Cα-Cβ bond follows one electron oxidation of **11** and produces vanillin (**4**) directly. This process is favoured over further one electron oxidation and deprotonation to give the α-carbonyl compound **12**. Note that this is not the case for model compound **1** where further oxidation to the α-carbonyl compound **8** is preferred to Cα-Cβ bond cleavage (mechanism K in Scheme 3). The stability of the radical formed on Cα-Cβ bond cleavage may have an important influence on the particular route these oxidation reactions take.

A possible alternative mechanism for the formation of vanillin (**4**) from **11** involves oxidation of the γ-carbon followed by a retro-aldol reaction.[20] However, in the absence of steric effects, α-carbon oxidation is expected to be more favourable than γ-carbon oxidation.

Loss of formaldehyde from **11** to give the vinyl ether **7** is a facile reaction and large quantities were formed in the control reactions. However, very little was isolated from the Fe(TSPc) catalyzed reactions, suggesting that the other pathways successfully compete with F'. In addition, Fe(TSPc) will partially degrade any **7** that forms (Table 2) thereby reducing the total amount isolated.

## EXPERIMENTAL

The conditions for the degradation reactions, the analytical techniques used and lignin model compound preparations have been described in Part I of this series.[1] Fe(TSPc) was prepared by a literature method.[21]

## CONCLUSIONS

Fe(TSPc) is an effective catalyst for the cleavage of guaiacol (**2**) from a number of lignin model compounds and, under the conditions used, it performs better than AQ. Whereas the Co(TSPP) and the AQ catalyzed reactions of **1** both give very similar product distributions, catalysis by Fe(TSPc) gives a different range of products. In particular, large amounts of the oxidized compounds **5** and **8** are formed. It is proposed this difference in reactivity arises because the oxidized form of the iron catalyst is capable of oxidizing **1** (and apocynol (**6**)) via an electron transfer mechanism to give the α-carbonyl **8** (and acetovanillone (**5**)). These reactions even proceed to some extent in the presence of added glucose. In contrast, AQ and $Co^{III}$(TSPP) are not strong enough oxidants to react this way and thus do not form these oxidized compounds to any appreciable extent. The formation of vanillin (**4**) in the Fe(TSPc) catalyzed reactions of **11** can also be rationalized in terms of an initial single electron oxidation. However, in this case Cα-Cβ bond cleavage then occurs to give vanillin (**4**) before further oxidation to the α-carbonyl compound **12** can proceed. Reaction of the reduced catalyst,

$Fe^I$(TSPc), with the quinone methide derived from **1** (or **11**) is an important route for guaiacol formation and provides a means for the oxidized form of the catalyst to be regenerated.

## ACKNOWLEDGEMENTS

The financial support of a Ph.D scholarship from PAPRO-NZ for P. A. Watson is gratefully acknowledged.

## REFERENCES

1. Part I of this series, J. Wood Chem. and Technol., this issue.
2. T. J. Fullerton, P. A. Watson and L. J. Wright, Appita, 43, (1), 23, (1990).
3. P. A. Watson, L. J. Wright and T. J. Fullerton, Tappi Proceedings of the 5th International Symposium on Wood and Pulping Chemistry, 75, 1989.
4. L. J. Wright and T. J. Fullerton, J. Wood Chem. and Technol., 4, (1), 61, (1984).
5. J. Gierer and I. Noren, Holzforschung, 36, (3), 123, (1982).
6. T. Habe, M. Shimada and T. Higuchi, Mok. Gakk, 31, (1), 54, (1985).
7. M. Shimada, T. Habe, T. Higuchi, T. Okamoto and B. Panijpan Holzforschung, 41, (5), 277, (1987).
8. A. Pasczynski, R. C. Crawford and R. A. Blanchette, Appl. and Envir. Micro, 54, (1), 62, (1988).
9. G. Labat and B. Meunier, J. Org. Chem., 54, 5008, (1989).
10. W. A. Nevin, W. Liu, M. Menik and A. B. P. Lever, J. Electroanal. Chem., 213, 217, (1986).
11. J. Gierer, O. Lindeberg and I. Noren, Holzforschung, 33, 213, (1979).
12. L. L. Landucci, Tappi, 63, (7), 95, (1980).
13. D. R. Dimmel, J. Wood Chem. and Technol., 5, (1), 1, (1985).
14. D. A. Smith and D. R. Dimmel, J. Org. Chem., 53, 5428, (1988).

15. R. D. Cosimo and H.-C. Szabo, J. Org. Chem., 53, 1673, (1988).

16. C. Walling, G. M. El-Taliawi, and C. Zhao, J. Org. Chem., 48, 4914, (1983).

17. J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, Principles and Applications of Organotransition Metal Chemistry", University Science Books, 1987.

18. P. A. Watson, L. J. Wright and T. J. Fullerton, Part III of this series, J. Wood Chem. and Technol. this issue.

19. J. Gierer and O. Lindeberg, Acta Chem. Scand., B32, 577 (1978).

20. R. Hise, C. -L. Chen, J. Gratzl, Proceedings of the Canadian Wood Chemistry Symposium, Niagara Falls, 1982, 21.

21. J. H. Weber and D. H. Busch, Inorg. Chem., 4, 469, (1965).