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Biomass electrochemistry: anodic oxidation of an organo-solv lignin in the presence of nitroaromatics

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The temperature required for the anodic conversion of an organo-solv spruce lignin, in aqueous alkaline solution, may be lowered by the addition of nitrobenzene or 1, 3-dinitrobenzene. The additives cause significant and reproducible changes in the Tafel plot for the reaction. Preparative-scale experiments are less reproducible although the range of phenolic products is generally similar to that produced by conventional nitrobenzene oxidation or by anodic oxidation at higher temperatures.

1. Introduction

Nitroaromatics, in alkaline solution, have long been used as oxidants [1] for organic substrates. Furthermore, useful reagents for the oxidative degradation of lignins to lower molecular products such as vanillin and syringaldehyde include alkaline nitrobenzene. This method is one of the standard procedures [2] for structural elucidation, by degradation, of lignins and related materials. The conditions are severe, requiring concentrated alkali and elevated temperatures (ca. 150–200° C), and analysis of the product mixture is complicated by the presence of aniline, phenylhydroxylamine, azobenzene, azoxybenzene and 4-hydroxyazobenzene (a product of rearrangement of azoxybenzene). Anodic oxidation is an alternative, and better, method for the degradation of lignins [3]. The electrochemical method essentially operates at ca 170° C, with a nickel anode and 3 M sodium hydroxide solution. At lower temperatures and in less alkaline conditions, oxidation of lignins (which are polymeric phenols) results not in degradation but in further intramolecular condensation.

The formation in the nitrobenzene method of by-products which are characteristic of electroreduction [4] of nitrobenzene suggests that the nitroaromatic compounds act as electron transfer oxidants. It follows that intermediates such as nitrosobenzene, known to be formed initially in nitrobenzene reduction [4], may be reoxidized electrochemically. Such oxidations have been little studied although Cauquis *et al.* [5] report that nitrosobenzene gives a well-defined oxidation wave on cyclic voltammetry.

We report herein on experiments which explore the possibility of anodically regenerating nitroaromatic oxidants in the presence of lignins and related compounds.

2. Experimental details

2.1. *Materials*

The acetone-soluble spruce lignin (ASPPS) has been described elsewhere [7]. We are grateful to Dr D. C. Ayres (QMC) for a gift of matairesinol (**2**). Borneol, camphor and vanillin were obtained commercially. Authentic samples or products, used for identification and calibration in HPLC analysis, were either purchased or synthesized by literature methods.

2.2. *Electrochemical experiments*

Solvents, electrolytes and apparatus were as described in earlier papers. The cell for electrolyses in aqueous alkali at 170° C was constructed of stainless steel and equipped with a PTFE liner (volume 50 cm^3); the top was also lined with PTFE and fitted with O-ring rubber seals and a safety valve (50 p.s.i.) This, and related cells, have been fully described elswhere [3]. The anode was a nickel gauze cylinder (size 40 mesh, 31 cm^2) and the cathode either a lead rod or a concentric lead foil cylinder.

Oxidations at lower temperatures (ambient) were in conventional undivided glass cells equipped with a nickel foil anode (18 cm^2) and a carbon plate of equivalent area.

Typical procedures, including the alkaline pretreatment are as follows.

2.2.1. Nitrobenzene oxidation of ASPPS (or of matairesinol). ASPPS or matairesinol (0.2 g) dissolved in 2 M aqueous sodium hydroxide (10 cm^3) was sealed in a stainless steel autoclave tube (volume 16 cm^3) and heated at 170–180° C with shaking at 15 min intervals for a total of between 1.5 and 4 h. The mixture was cooled, nitrobenzene (2.4 g) added, the autoclave tube re-sealed and heating continued at 170–180° C for a further 3 h. After cooling in ice, the contents were shaken with ether to remove the unwanted nitrobenzene reduction products. The residual alkaline solution was acidified (conc. HCl to pH 3) and the remaining organic products extracted into ether and analysed (HPLC, details below).

2.2.2. *Anodic oxidation of ASPPS*

(i) High temperature, no additive: lignin (ASPPS, 0.25 g) was dissolved in aqueous sodium hydroxide ($25\,cm^3$, 3 M) and introduced into the electrolysis cell prior to sealing. The cell was heated to 170° C and electrolysis was continued at $4\,mA\,cm^{-2}$ for 4 h, during which 10^3 coulombs was passed. The contents were magnetically stirred. The voltage required was always less than 5 V, usually 1.8–2.0 V. The cell was then cooled, pressure released and the contents decanted off. The contents were then acidified to pH 2 with hydrochloric acid. The acid mixture was shaken with chloroform (3 × 70 × 1) and the chloroform layer separated off, neutralized with sodium carbonate and dried with sodium sulphate.

Filtration and evaporation yielded a light brown semi-solid product (0.09 g, 36% yield by weight). Analysis of this product by chromatographic methods showed that the major products were:

	Relative yield (mol %)
Vanillic acid	19
4-Hydroxybenzaldehyde	51
Vanillin	17
4-Hydroxyacetophenone	9
Acetovanillone	4
(Plus 2 unidentified products)	

(ii) High temperature, added nitrobenzene: after the usual alkaline pretreatment (ASPPS (0.2 g), 2 M NaOH ($10\,cm^3$))nitrobenzene (0.12 g) in 2 M NaOH ($40\,cm^3$) was added and the solution electrolysed at 170–180° C and $2\,mA\,cm^{-2}$ for 3 h in the pressurized cell. The products were analysed as before.

(iii) Ambient temperature added nitroaromatic: after the usual alkaline pretreatment (ASPPS (0.2 g), 2 M NaOH ($20\,cm^3$)) a further $50\,cm^3$ of 2 M NaOH was added together with nitrobenzene (0.24 g) or 1, 3-dinitrobenzene (0.08 g). The stirred electrolyte was electrolysed at $4\,mA\,cm^{-2}$ in the undivided cell described above and products analysed as before.

2.3. *Analysis*

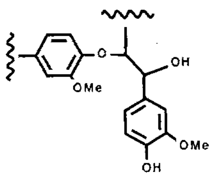
The mixtures of phenolic compounds were analysed by gradient elution HPLC with u.v. detection of eluants at 280 nm. For nitrobenzene oxidation it was first necessary to remove 4-hydroxyazobenzene, a significant and interfering by-product, by chromatography as before through silica gel (Kieselgel-60 PF). The azobenzene derivative was eluted with petrol (b.p. 40–60° C)–ethyl acetate (3 : 1 v/v) and the phenolic products with ethyl acetate.

The HPLC detector was calibrated by the analysis of mixtures of authentic samples with a known composition. Suitable conditions were found to involve the use of a C-18 microbondapak, reverse phase column 25 cm × 4 mm i.d.) with 1% aqueous $NH_4(H_2PO_4)$/methanol; in a typical run the solvent composition would change from 10 to 100% methanol during 65 min.

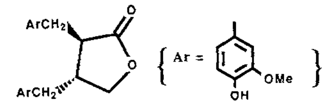
3. Results and discussion

3.1. *Materials*

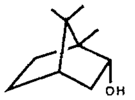
Lignins are mixtures of complex three-dimensional polymers of hydroxylated and methoxylated arylpropane (C_9) units. The major structural features are known [6]. We have chosen to work with a well-characterized [7] organo-solv lignin, the acetone-soluble phenol-pulping spruce (*Picea abies*) lignin (ASPPS). High field ^1H and ^{13}C NMR spectroscopy confirm [7] that α-hydroxyl and β-*O*-aryl ether functions, with *erythro* stereochemistry, are prominent in this material and a convenient representation of the most important repeat units is **1**. For comparisons of reactivity towards the several oxidation regimes explored, matairesinol (**2**), borneol (**3**) and vanillin (**4**) have been used as substrates. Matairesinol contains the easily oxidized phenolic moeity of the lignin but without the α- and β-oxygen functions; borneol is an example of a secondary alcohol which may be oxidized to camphor (**5**) by alkaline nitrobenzene, at > 150° C.



(**1**)



(**2**)



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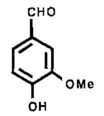
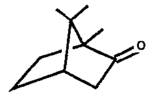


(**4**)



(**5**)

3.2. *Anodic and chemical oxidation*

The presence of nitroaromatics, specifically nitrobenzene and 1, 3-dinitrobenzene, causes a dramatic reduction in the temperature at which anodic degradation of the ASPPS lignin occurs. Low-temperature (ca 25° C) anodic oxidation in alkaline solution at nickel results in further condensation in the absence of nitroaromatic. In contrast, for some experiments in the presence of nitroaromatic, oxidation proceeded to the carbon dioxide level; in others, useful conversion into vanillin (**4**) and 4-hydroxybenzaldehyde (**6**, 4-HBA) was achieved. The results of key experiments are summarized in Table 1; they are presented for

*Table 1. Nitroaromatic oxidation of matairesinol (**2**) and lignin (ASPPS) with and without coelectrolysis*

Entry	*Substrate*	*Conversion Method*	*Relative yields (%)*[a]				*Total product yield (w/w%)*[b]
			*4-HBA (**6**)*	*Vanillin (**4**)*	*Phenol*	*Others*	
1	Matairesinol (**2**)	$PhNO_2^c$	–	(1.8%)[g]	–	–	
2		$PhNO_2^e$	–	(8.8%)[g]	–	–	
3		1, 3-DNB[e]	–	(5.3%)[g]	–	–	
4		$PhNO_2$, coelectrolysis[f]	–	(12%)[g]	–	–	
5		$PhNO_2$ coelectrolysis[e,f]	–	(18%)[g]	–	–	
6	ASPPS	$PhNO_2^c$	34	41	8	17[d]	26
7		$PhNO_2^e$	30	30	5	35[h]	17.5
8		1, 3-DNB[e]	22	28	13	37[i]	18
9		$PhNO_2$, coelectrolysis[j]	12	18	8	62[k]	0.36
10		$PhNO_2$, coelectrolysis[l]	30	23	26	21[m]	29.6
11		$PhNO_2$, coelectrolysis[l]	7	74	–	19[n]	2.0
12		$PhNO_2$, coelectrolysis[l]	1	23	72	4[p]	13.0
13		$PhNO_2$, coelectrolysis[l]	1	28	10	61[q]	8.0
14		1, 3-DNB, coelectrolysis[l]	5	5	4	86[r]	2.0
15		1, 3-DNB, coelectrolysis[l]	11	30	12	47[s]	50.0
16		1, 3-DNB, coelectrolysis[l]	18	13	41	28[t]	28.0

[a] By HPLC, relative molar yields.

[b] Expressed as W/W% because of uncertainty in lignin molecular formula.

[c] Substrate (0.05–0.2 g), 2 N aq. NaOH, 170–180° C, 2.5–4 h.

[d] Phenol, vanillic acid, quaiacol and acetovanillone (each ca 4%).

[e] After pre-treatment (see experimental section).

[f] Substrate (0.2 g), $PhNO_2$ (0.24 g), electrolysis as in (**1**).

[g] True yields, not relative.

[h] Syringaldehyde (4-hydroxy-3, 5-dimethoxybenzaldehyde, 21%) vanillic acid (4-hydroxy-3-methoxybenzoic acid, 3%), guaiacol (2-methoxyphenol, 4%), 4-hydroxybenzoic acid (6%), acetovanillone (4-hydroxy-3-methoxyacetophenone, 3%).

[i] Vanillic acid (13%), guaiacol (10%), syringaldehyde (8%), 4-hydroxybenzoic acid (6%).

[j] No pre-treatment, substrate (0.2 g), sealed cell, Ni gauze anode, Pb cathode, 2 N aq. NaOH, 170–180° C, 0.2 mA cm^{-2}, 3 h.

[k] Mainly polymer, traces of 4-hydroxybenzoic acid.

[l] Ambient temperature, Ni foil anode, carbon cathode, 4 mA cm^{-2}, 3 h.

[m] Guaiacol (12%), 4-hydroxybenzoic acid (6%), vanillic acid (3%).

[n] Polymerization, vanillic acid (19%).

[p] Acetovanillone (3%), traces of 4-hydroxybenzoic acid and 4-hydroxyacetophenone.

[q] Syringaldehyde (21%), acetovanillone (18%), vanillic acid (18%), guaiacol (4%).

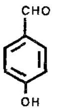
[r] Evolution of CO_2 on acidification, major product 4-hydroxybenzoic acid (50%) and acetovanillone (23%).

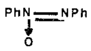
[s] Guaiacol (27%), 4-hydroxyacetophenone (20%).

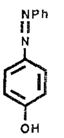
[t] Mainly syringaldehyde (9%), 4-hydroxybenzoic acid (6%) and guaiacol (5%).

individual experiments to illustrate the range of results to be expected. The problems of reproducibility with an inherently heterogeneous system have not been solved. In the electrolyses it is commonly observed that low conversion to degradation products is accompanied by conversion of the lignin into a less soluble, probably more condensed, form.

Especially noteworthy from the results in Table 1 and for additional experiments is: (a) pretreatment of the lignin with 2 M NaOH at 180° C is necessary, although this does not itself cause breakdown to low molecular weight products; (b) the proportion of **6** : **4** is high; (c) 1, 3-dinitrobenzene is a more effective additive than nitrobenzene: (d) the nitrobenzene oxidations, with and without coelectrolysis, give azoxybenzene (**7**) and 4-hydroxyazobenzene (**8**) as byproducts; (e) matairesinol (**2**) is less efficiently oxidized than the lignin; (f) borneol (**3**) is not oxidized by nitrobenzene at up to 80° C; and (g) vanillin (**4**) is significantly demethoxylated to give 4-HBA (**6**) when vanillin is pre-heated in 2 M NaOH at 180° C. In an electrochemical experiment performed without pretreatment only traces of the demethoxylated product were found.


(**6**)

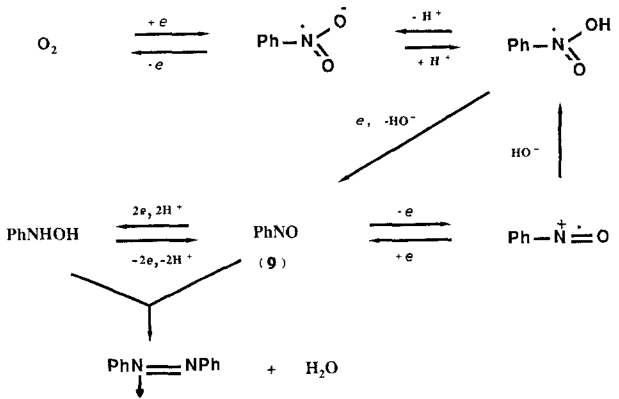

(**7**)


(**8**)

The formation of azoxybenzene (**7**) and the product of its rearrangement (**8**) indicate that nitrobenzene effects oxidation via initial electron transfer and is itself reduced. What is known [4] of nitroaromatic reduction pathways at high pH suggests the redox cycle given in Scheme 1.

The successful experiments summarized in the Table 1 were undertaken with the hope that continuous regeneration by oxidation of nitroaromatic would be possible, the formation of the toxic and inconvenient nitrogenous byproducts avoided, and low concentrations of oxidant employed. However, in a separate experiment no evidence was found, by GLC analysis, for regeneration of nitrobenzene by anodic oxidation of nitrosobenzene (**9**) in alkaline solution.

In aprotic solvents, e.g. acetonitrile and nitromethane, anodic oxidation of nitrosobenzene (q) into its radical cation has been demonstrated [5]. Our



Scheme 1

experiments show that, according to cyclic voltammetry at a platinum anode in $CH_3CN\text{-}Bu_4BClO_4$ (0.1 M), nitrosobenzene (**9**) gives a single, irreversible, oxidation peak at 1.1 V (vs Ag/Ag^+); this is considerably more anodic than the corresponding value (0.5 V) for oxidation of matairesinol (**2**) under similar conditions. The latter may be taken as characteristic of the oxidation behaviour of lignins.

Voltammetric curves obtained with the cell, electrodes and electrolytes used for preparative electrolysis also confirm that it is unlikely that conditions for reoxidation of nitrosobenzene (**9**) prevail at the relatively low current densities used (Fig. 1). According to Fig. 1 the major effect of nitrobenzene addition is the displacement of the lignin oxidation curve to more positive potential for a given current density. The results displayed in Fig. 1 were obtained, for stirred solutions, under conditions identically matching those for the successful lignin degradations. These results were reproducible for several separate experiments and, for a given electrolyte, the same curves resulted either by varying current density and measuring the steady state potential or by varying potential and measuring the steady state current. This proof of reproducibility is important because both nitrobenzene and 1, 3-dinitrobenzene are sparingly soluble in 2 M aqueous sodium hydroxide and, in the absence of lignin, it is unlikely that the electrolyte is homogeneous. The outcome of preparative experiments was not so predictable. However, the phenolic lignin is readily soluble in 2 M sodium hydroxide and such a solution is likely to act as a detergent and solubilize the nitroaromatic. This solubilization will also be aided by the well-known [8] propensity of aromatic nitro compounds to form complexes with electron-rich aromatics, including phenols.

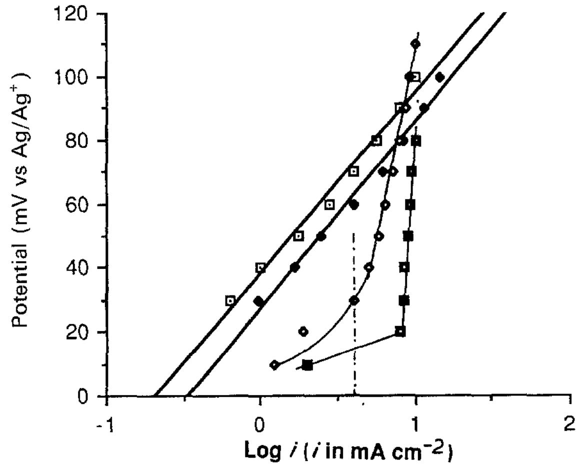


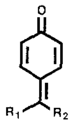
Fig. 1. Effect of additive on Tafel plot. ▫ 2 N Aqueous NaOH, ◆ 2 N Aqueous NaOH plus $PhNO_2$, ◇ 2 N Aqueous NaOH plus ASPPS lignin, ▪ As above, plus $PhNO_2$, ---- Current density for preparative electrolyses.

3.3. *Mechanistic rationalization*

The inertness of borneol (**3**) in conditions which degrade lignin strongly suggests that oxidation is not indirect and initiated by H-atom abstraction; this mechanism is known to be important for the oxidation of alcohols [9]. Matairesinol (**2**) is not converted into vanillin (**4**) as efficiently as is the lignin so electron transfer from the electron-rich 3-methoxy-4-hydroxyphenyl group is not the sole criterion for success.

A working hypothesis for the mechanism can however be developed following definition of the role of the essential alkaline pre-treatment and assumption that α-hydroxylation aids degradation (matairesinol cf. lignin). Other established features to be accommodated in an hypothesis are that the better oxidant (1, 3-dinitrobenzene) is the more effective additive. Alternative roles for the nitroaromatic are that it either introduces a reaction which competes well with further condensation or that it retards such condensation.

There is much evidence [10] that quinonemethides (e.g. **10**) are crucially involved in both the formation and cleavage of lignins. Furthermore, in at least one case [11] reductive cleavage of a lignin model compound has been effected by redox catalysis involving the corresponding quinomethide and anthraquinone radical anion.

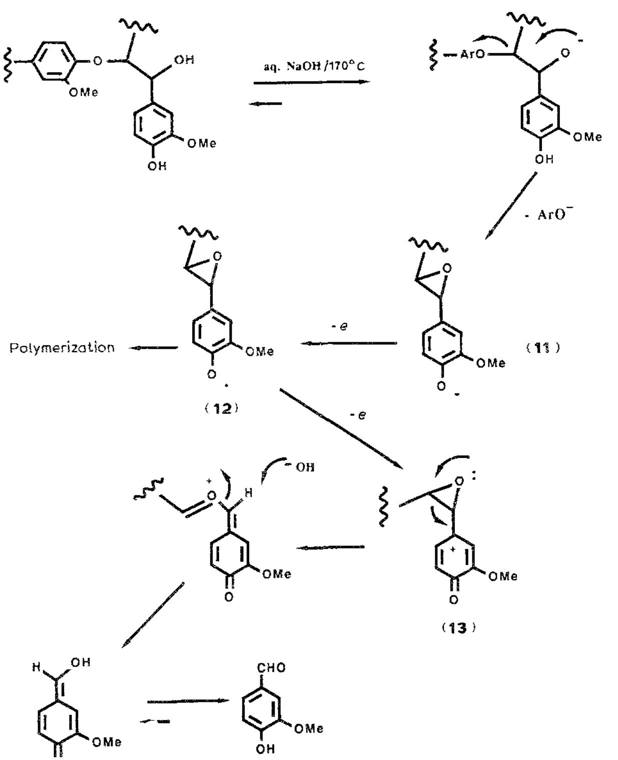


(**10**)

These considerations are combined in the pathways proposed in Scheme 2. The suggestion that alkaline pre-treatment involves the α-hydroxyl function and conversion into an epoxide is strongly supported by precedent. Conversion of a lignin model compound into the corresponding epoxide (**11**) (scheme 3), resulted [12] from reaction in aqueous sodium hydroxide (2 M) at 170° C, the same conditions used in our experiments.

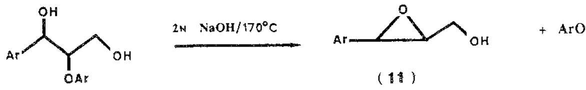
The formation by anodic oxidation of phenoxyl radicals (**12**) and of phenoxonium cations (**13**) is also well established [13]; indeed, the formation of lignin in nature is believed to involve combination of phenoxyl radicals produced by enzymatic oxidation. Quinonmethides also react [14, 15], unless highly hindered, to give polymers.

Finally, the carbon–carbon bond cleavage driven by the 1, 3 disposition of a carbocationic centre and oxygen has good precedent [15] in the fragmentation

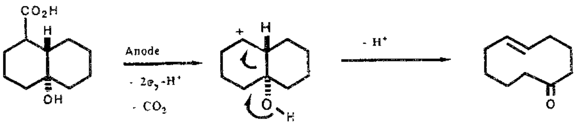


Scheme 2

given in scheme 4. The mechanistic suggestion summarized in Scheme 2 is therefore consistent with the evidence so far obtained, explains oxidation to the aldehyde level (the predominant reaction), and is powerfully supported by literature precedent.



Scheme 3



Scheme 4

However, the role of added nitroaromatic has not been explained and can only be the subject of speculation. The displacement of the Tafel curves (Fig. 1) suggests a modification of the electrode condition, usually the last refuge of the confused electrochemist, or interaction between the lignin and additive. In the absence of additive the nickel anode is operating under conditions normally associated [16] with Ni(III) oxide formation. Oxidation under these conditions, however, rarely stops at the aldehyde level. In some experiments significant overoxidation was observed, even to the carbon dioxide level. These observations would be consistent with oxidation by Ni(III) oxide; complete oxidation to carbon dioxide would also be expected following the observation [18] that lignin-model quinones are oxidized by alkaline hydrogen peroxide to mixtures of low molecular weight mono- and dicarboxylic acids which would certainly decarboxylate anodically.

The nitroaromatic could possibly intercede in the pathways given in Scheme 2 by facilitating the second electron transfer. Such an explanation involves the further assumption that polymerization is mainly via phenoxyl radicals and cleavage via phenoxonium cations. The aromatic nitrocompound might by active via adsorption or concentration at the anode, or by specific complexation with the phenolic substrate. Such complexation is well known [8] for phenols and nitroaromatics and would explain the reproducibility of the curves in Fig. 1 for a system which would otherwise be expected to be heterogeneous (see above). The greater effectiveness of the better oxidant (1, 3-dinitrobenzene) follows. Alternatively the second electron transfer may be facilitated simply because the additive causes, at a given current density, a shift to more anodic potentials by whatever mechanism. In the successful experiments the amount of nitroaromatic additive was roughly equivalent to the amount of lignin.

Acknowledgements

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