[7] K. B. Oldham, J. C. Myland, C. G. Zoski and A. M. Bond, J. Electroanal. Chem., 79-101.

[8] A. Ehrenberg, Acta Chem. Scand., 11 (1957) 1257-1270.

[9] K. Niki, T. Yagi, H. Inokuchi and K. Kimura, J. Am. Chem. Soc., 101 (1979) 3335-3340.

[10] J. B. Flanagan, S. Margel, A. J. Bard and F. C. Anson, J. Am. Chem. Soc., 100 (1978) 4248-4253.

[11] M. V. Mirkin and A. J. Bard, J. Am. Chem. Soc., 64 (1992) 2293-2302.

ELECTROOXIDATION OF LIGNIN IN ALKALINE MEDIUM

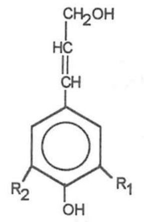
E. M. Belgsir[2], A.P. Bettencourt[1], A. M. Carvalho and P. Parpot[1*]

1Departamento de Química, Universidade do Minho, Largo do Paço, 4709 Braga Codex, Portugal.
2Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, 40, Avenue du Recteur Pineau, 86022, Poitiers France.

Abstract: The electrochemical behavior of lignin, in alkaline medium, was studied by cyclic voltammetry and compared with that of some lignin model compounds e. g. guaiacol, eugenol, vanillic alcohol and vanillin, in order to elucidate the process involved in electrode reactions. Galvanostatic electrolyses of lignin were carried out using different electrode materials in order to investigate the influence of electrode material on the product distribution.

Introduction:

According to the widely accepted concept, lignin may be defined as an amorphouse polyphenolic material arising from an enzyme mediated dehydrogenative polymerization of three phenylpropanoid monomers, coniferyl (1), sinapyl (2), and p-coumaryl (3) alcohols [1].



(1) $R_1 = OCH_3$; $R_2 = H$

(2) $R_1 = R_2 = OCH_3$

(3) $R_1 = R_2 = H$

The estimated annual production of lignin as a by product of paper making industry is about 30 millions tons. 95% of this amount are burned or dumped as polluting effluent and only 5% are converted into useful chemicals [2]. Electrochemistry of lignin has ben the subject of numerous studies including the depolymerization, the preparation of new polymers for special applications and the conversion into useful compounds [3].

The aim of this work is to evaluate the performance of the electrochemical way in low molecular weight carbonyl compounds production from the oxidative degradation of lignin.

Experimental :

Electrochemical equipment

The preliminary studies were carried out by cyclic voltammetry. The voltamograms were recorded using a PPRI model waveform generator (HI-TEK) a DT2101 model potentiostat (HI-TEK) and a PM 8043 model XY recorder (Philips). A thermostated three-electrode electrochemical cell was used. A saturated calomel electrode (SCE) served as a reference electrode but all the potentials are given in the reversible hydrogen electrode (RHE) scale. The counter electrode was a platinum grid. Discs of platinum, gold, nickel and vitreous carbon were used as working electrodes. All the electrode activities are given in current densities, the active area being estimated from the hydrogen adsorption for the platinum electrode and the oxygenated species reduction for the gold electrode. For the nickel and carbon electrode the current densities are referred to the geometric area. The electrodes were polished using 0,3 μm aluminum oxide. The supporting electrolyte was prepared from ultrapure water (E-pure system) and analytical grade NaOH (Pronalab). Lignin, vanillin and eugenol were supplied by Aldrich. Guaiacol and vanillyl alcohol were also supplied by Aldrich. Before each experiment the solutions were dearated with ultrapure argon (R quality from L'Air Liquide) while a argon stream was maintained over the solution during the experiment. Cleanless of electrode surfaces and solutions was tested prior to each experiment by recording voltammograms in the supporting electrolyte alone.

The laboratory scale electrolyses of lignin and guaiacol on platinum were carried out in a two compartment glass cell separated by an ion exchange membrane (IONAC AM 3470 from Sybron Chemicals). A saturated calomel electrode (SCE) and a 90% platinum/10% iridium sheet served as reference and counter electrode, respectively.

The FM01-LC flow cell supplied by ICI Chemicals and Polymers and the ElectroCell AB micro flow cell supplied by ElectroCell were used to perform the scale up electrolyses. The anolyte and the catholyte were circulated separately by a Watson-Marlow peristaltic pump. Two compartments were separated by an ion exchange membrane (IONAC AM 3470). The galvanostatic electrolyses were performed using a DC stabilized power supply (IKA-EN 500) and a galvanostat/potentiostat (AMEL 2055). The flat plate nickel, DSA (dimensionally stable anode i.e. RuO_2 based coatings on Ti) and lead electrodes were used as working electrode and the stainless steel plate as counter electrode.

Analytical equipment

Gas chromatography (GC) was performed with a Varian gas chromatograph using a DB-5 capillary column (95% dimethyl-5% diphenyl-polysiloxane bonded, 30 m, 0.25 mm i.d. and 0.25 μm film thickness). This was combined with a mass spectrometer (INCOS 500).

Results and Discussion:

Cyclic Voltammetry

The electrochemical properties of lignin model compounds were investigated in alkaline medium (0.1M NaOH) on platinum, gold and nickel electrodes and compared with those of lignin by cyclic voltammetry. The electrochemical data related to model compounds and to lignin are summarized on Tables **1**, **2**.

Electrode	Ep (V/RHE)	j (mA.cm^{-2})	ΔH* (kJ. mol^{-1})	∂log i/∂log v
Pt	1.17	0.35	17	0.5
Au (1st peak)	1.18	0.20	21	0.4
(2nd peak)	1.50	0.12	15.3	0.6
Ni (1st peak)	1.38	0.24	24	0.6
(2nd peak)	1.57	0.28	10.3	0.6
C (vitreous)	1.18	0.36	15.7	0.5

Table 1. Electrooxidation of lignin in alkaline medium: Effect of electrode material on the peak potentials, on the maximum current densities, on the apparent energy of activation and on the log i = f(log v) slopes.

Model compounds	Ep (V/RHE)			j (mA.cm^{-2})		
	Pt	Au	Ni	Pt	Au	Ni
guaiacol	1.25	1.23	1.33	1.8	0.7	1.7
eugenol	1.18	1.17	1.28	0.7	0.3	1.8
vanillin	1.63	1.63	1.78	3.0	2.4	22.4
vanillic alcohol	1.25	1.05	1.28	1.3	0.7	0.7
		1.24	1.49		1.0	0.7

Table 2. Electooxidation of model compounds of lignin in alkaline medium. Effect of electrode material on the peak potentials and maximum current densities.

The first remark concerns the quasi identical peak potential values of guaiacol, eugenol, vanillic alcohol (2nd peak) and lignin. It seems that the process involved at these potentials correspond to the oxidation of the phenolate anion. In the case of vanillic alcohol the first peak is attributed to the oxidation of the primary alcohol group. The second remark concerns the more positive values of vanillin oxidation peaks and the relatively high current densities obtained at nickel electrode.

In presence of lignin, the deactivation of the electrode is less drastic than that observed with its model compounds. However, current densities are perceptibly lower and their maxima are not affected by the nature of the electrode material. The apparent energies of activation estimated for all the investigated electrodes correspond to a process rather controlled by diffusion. This is confirmed by the log i = f(log v) slope values, closed to 0.5. Moreover, as for the model compounds, the experimental number of electron during the first oxidation wave is equal to unity.

Electrolyses

Galvanostatic electrolyses were carried out, using nickel, lead oxide and dimensionally stable anode (DSA) in "filter-press" type flow cells (FM01-LC from ICI and ElectroCell AB from ElectroCell). The anolyte solution contained 0.5 % lignin in 1M NaOH and its circulation was separated from the catholyte one, which contained just the supporting electolyte alone (1M NaOH).

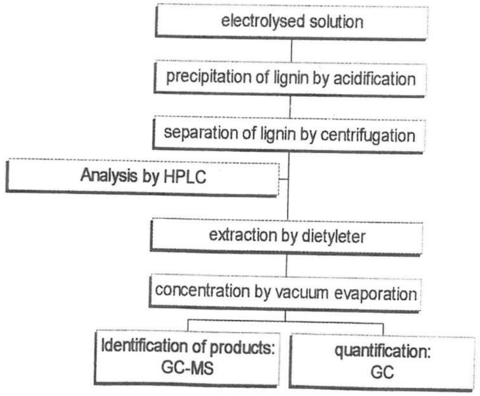


Figure 1. Preparation of samples for analysis

The solutions were electrolysed during three hours, at room temperature with current densities about 0.03 $A.cm^{-2}$. After precipitation of the remaining lignin the oxidation products were extracted by diethyl eter. The extracted products were identified by GC-MS coupling and quantified by GC (Fig.1).The percentages of the extracted products are reported on **Table 3**. The resulting reaction mixtures show slight differences.

	Ni (%)	**PbO_2** (%)	**DSA** (%)
Guaiacol	16	12	8
Hydroxymethoxyphenyl ethanone	12	11	15
Hydroxybenzaldehyde	4	2	2
Vanillin	56	64	63
Vanillic acid	5	4	1
Hydroxymethoxybenzene acetic acid	5	5	8

Table 3. Electrooxidation of lignin in alkaline medium: effect of electrode material on the product distribution.

References:

[1] S. Y. Lin, C. W. Dence, *Methods in Lignin Chemistry*, Spring Series in Wood Science, Springer-Verlag Berlin Heidelberg, 1992

[2] J.H.P. Utley, *Spectrum*, 212 (1988) 2

[3] M. Baizer, H. L. Chum, *The Electrochemistry of Biomass and Derived Materials*, ACS Monographs, 1985.

Acknowledgments: this work was supported by JNICT throught PBIC/C/QUI/2203/95. The authors are grateful to ICI Chemicals and Polymers Ltd. for a loan of the FM01-LC flow cell.

ELECTROSYNTHESIS OF STILBENE - EFFECT OF EXPERIMENTAL PARAMETERS ON THE REACTION YIELD AND STEREOCHEMISTRY

A. P. Bettencourt, A. M. Freitas, M. I. Montenegro* and P. Parpot

Departamento de Química, Universidade do Minho, Largo do Paço
4709 Braga Codex, Portugal

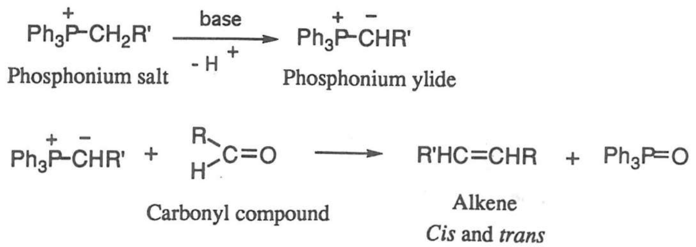
ABSTRACT

The influence of experimental parameters on the yields and stereochemistry of Wittig reaction was studied. The synthesis of stilbene initiated by different electrogenerated bases was used as a model reaction. Preparative electrolyses were carried out in different conditions including constant potential or constant current with different electrode materials and using solvents of different polarity. Both the yield and the stereochemistry of the reaction are affected by the electrolysis experimental conditions. Hence, the proper selection of experimental conditions in Wittig reactions allows the choice of the stereosselectivity of the reactions and the optimization of yields.

Keywords: Electrogenerated bases, Wittig reactions, Electrosynthesis

INTRODUCTION

The synthesis of unsaturated compounds is commonly carried out by Wittig reactions [1,2]. This reaction involves the condensation of a phosphorous ylide and a carbonyl compound, according to scheme 1:



Scheme 1 - Wittig reaction.

Portugaliæ Electrochimica Acta, 15 (1997) 417-422