ELECTROCHEMICAL INVESTIGATIONS OF ALKALINE CLEAVAGE OF LIGNIN UNDER MILD CONDITIONS

Petr ZUMAN[1],* and Elinore B. RUPP[2]

Department of Chemistry, Clarkson University, Potsdam, NY 13699-5810, U.S.A.;
e-mail: [1] zumanp@clarkson.edu, [2] erupp@stlawu.edu

At pH 8–12 and 25 °C, 10–20% of lignin undergoes cleavage producing soluble species. In suspensions of lignin it is possible to follow the concentration changes of hydroxybenzaldehydes and α,β-unsaturated carbonyl compounds. These species can be determined by the recording of polarographic current–voltage curves directly in the suspensions, where the presence of suspended and colloidal particles does not interfere with the function of the DME. The base-catalyzed cleavage follows first-order kinetics. The pH dependence indicates that the rate determining step is not a nucleophilic attack by OH^-, rather the rate determining step is preceded by a rapidly established acid–base equilibrium. The cleavage of natural lignins obtained enzymatically follows a pattern similar to that of rot wood lignins and surprisingly also to that of kraft lignins. The patterns of cleavages are different from those of lignosulfonates, Klason, periodate and expansion lignin. The three dimensional (tertiary) structure of lignin seems to play a role in its reactivity.

Keywords: Lignins; Lignans; Hydrolysis; Polarography; Phenols; Aldehydes; Hydroxybenzaldehydes.

During the last two decades, the number of applications of polarography in practical analysis decreased considerably. Nevertheless, there are some areas where polarography still fulfils the conditions to be the best method for the solution of a given analytical problem. One of such areas is the analysis of heterogeneous systems. This is facilitated by the low sensitivity of limiting currents obtained by DC or normal pulse polarography to the presence of colloidal or dispersed, slightly soluble particles. It is thus possible to carry out, without separation other than that of the largest particles, direct analyses in real time of electroactive species in the presence of colloids and solid particles. An example of such applications is the determination of electroactive species in suspensions of lignin.

Lignin promises to be one of the materials of the future. The chemical industry was first based on coal and now relies on oil as the single most important raw material. Eventual exhaustion of oil and later of coal will have

repercussions not only in the generation of energy, but also on the change of the selection of raw materials for the chemical industry. Abundant, cheap, renewable raw materials will be needed. Moreover, the processing of such raw materials should involve low energy demands. Whereas for the generation of energy, extraterrestrial sources are considered, carbohydrates seem to be the most promising materials for syntheses of aliphatics and some heterocyclics; lignin seems to fulfil the role of a most suitable source of aromatics.

Lignin is – after carbohydrates – the second most frequently encountered organic polymer on the surface of the Earth. Wood, straw, and similar parts of plants contain between 10 and 30% of lignin. Natural lignin is a complex, water-insoluble three-dimensional polymer of molecular weight of more than 100,000. It consists predominantly of 3-phenylpropane subunits, which are more or less randomly linked. An idealized two-dimensional picture of the structure of lignin is shown in Fig. 1. By the random linkage of the 3-phenylpropane units substituted with hydroxy, alkoxy, or carboxy groups, lignin differs from most naturally occurring polymers (like proteins, celluloses, gums, *etc.*) which contain repeating structure units. There is some similarity in the structure of lignins from individual members of a given family of plants, but usually only an "overall structure" is known. Studies of adsorption of inorganic[1,2] and organic[3–10] species on lignins indicated that individual lignins differ considerably in their three-dimensional (tertiary) structures.

In industrial applications, lignin is mostly considered an unwanted component which must be removed from the product. This is particularly true about paper manufacture and in obtaining materials for the synthesis of cellulosics for the polymer industry. In industrial processes, lignin is separated from wood under drastic conditions, such as strongly alkaline media (usually in the presence of 1 M or higher concentration of hydroxide ions), at high temperatures (often above 100 °C) and at high pressure. Under such conditions, the goal is achieved of removing all lignin completely from cellulose. Such conditions are, nevertheless, unsuitable for obtaining useful intermediates for organic syntheses. Under extreme conditions used in commercial processes aimed at the removal of lignin from cellulose, low-molecular-weight products formed can namely undergo numerous consecutive reactions, including – but not restricted to – Cannizzaro-type reactions, aldol formation, Michael-type additions, oxidation with air, *etc.* Furthermore, repolymerization can occur yielding oligomers and polymers different from the parent lignin. Aldehydic groups, present under these

conditions at least partly as geminal diols, can be easily oxidized with molecular oxygen to carbohydrates.

In the course of our investigations of adsorption of various species on lignin[1-10], we observed that whereas at pH < 7 lignin in suspension is stable for hours and days, at pH > 8 changes in suspended lignin take place with time, resulting in the formation of gradually increasing amounts of water-soluble species. This cleavage of lignin occurs already at 25 °C.

During the investigations of suspensions of lignin, we confirmed that the properties and reactivity of lignins somewhat depend on the source of lignin[1-6]. Moreover, we observed that the properties of lignins depend very
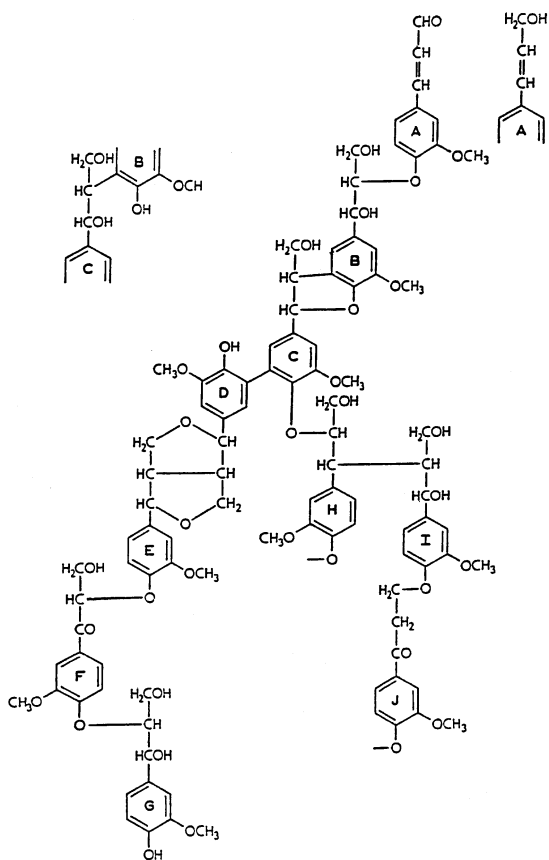

Fig. 1
An idealized, two-dimensional structure of lignin, indicating various types of bonding of the phenylpropane units

much on the way in which a given lignin is separated from carbohydrates and processed. Already the process of comminution of wood plays an important role. Thus the properties of lignin prepared from wood pulverized with a Hurricane Pulverizer (a hammer mill) differ from those of lignin obtained when the wood was treated in a Wiley mill (a rotating steel cutter)[4]. Furthermore, an increased temperature during comminution (later controlled by cooling to 25 °C) and the composition of the blades (affecting the level of metal traces in the produced lignin) proved to be of importance[4]. In order to obtain samples of lignin as close to its natural state as possible, ceramic ball mills were used. To separate lignin from carbohydrates like hemicellulose, a mixture of cellulases produced by cultures of *Schizophyllum commune* and *Trichoderma resei* was used, as well as cellulases produced by cultures of *Trichoderma viride* (Cellucast). The role of metal ions derived from culture media on properties of lignin was considered[4]. The role of washing lignin preparations with aqueous solutions and of extraction with organic solvents was investigated[3], as well as that of ionic strength[1,4] and the nature of the cations of neutral salts and buffers present in the suspension[4].

The reactivity of lignins obtained by microbiological techniques increased with decreasing content of carbohydrates in the sample and hence only lignins containing less than 4% of carbohydrates were used in the reported studies. Lignins obtained by microbiological procedures were reactive, but available only in small amounts. In the search for lignins available in larger amounts, we excluded lignosulfonates, periodate lignin, Klason lignins, organosolv-lignins, as well as lignins obtained by rapid expansion, as all of these have properties different from those of natural lignins. Nevertheless, we found two materials, the properties of which resembled those of lignins, prepared by microbiological procedures. Lignin prepared by digestion using Cellucast from brown rot wood by decaying it with *Polyporus betulinum* was shown to have properties similar to other enzymatically produced lignins. More importantly, rot-wood lignin was shown to have properties similar to those of naturally rotted wood[1,4]. Collected rotted wood thus represented an abundant source of lignin for our studies. The second useful material proved to be – to our surprise – kraft soft wood lignins, both original, prepared by heat coalescence and spraying, and acetylated[3]. As the tertiary structure seems to be of importance for the reactivity of lignins, it can be speculated that the tertiary structures of kraft lignin resemble those of natural lignins, with sulfidic and disulfidic bonds involved in the generation of a three-dimensional structure, somewhat resembling that in natural

lignins. As rot-wood and kraft lignins are available in larger quantities, we have chosen them for the studies of lignin cleavage.

EXPERIMENTAL

Instrumentation

The DC current voltage curves and differential pulse polarographic (DPP) curves were recorded using a Sargent–Welch Mark 4001 polarograph with a controlled drop time of 1 s. DPP curves were recorded using an excitation signal Δe = 50 mV and a controlled drop time (1 s). The dropping mercury electrode used had m = 3.01 mg/s and t_1 = 2.9 s at h = 73.5 cm in a 0.1 M KCl at 0.0 V (SCE). The curves were recorded with h = 56 cm. Polarographic studies were conducted in a Kalousek cell using a saturated calomel electrode separated by a liquid junction as a reference.

Measurements of pH were carried out with a PHM 84 Research pH meter (Radiometer) with a G202B glass electrode and a K422 saturated calomel electrode, both from Radiometer. UV absorption spectra were recorded with a Perkin–Elmer spectrometer Mark 559.

Chemicals and Solutions

Vanillin (4-hydroxy-3-methoxybenzaldehyde) (99%), syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) (98%), isovanillin (3-hydroxy-4-methoxybenzaldehyde) (99%), 4-hydroxybenzaldehyde (98%), and *trans*-cinnamaldehyde ((*E*)-3-phenylprop-2-enal) (99%) were all obtained from Aldrich Chemical Company and used without further treatment.

Chemicals used for the preparation of buffers were analytical or reagent grade and used as supplied. Acetate buffers were prepared by mixing solutions of acetic acid and sodium acetate in varying proportions, keeping the total analytical concentration of acetic acid 0.2 mol/l. To prepare phosphate buffers pH 3, 5–8, and 10.5–12, solutions of phosphoric acid, potassium dihydrogenphosphate, dipotassium hydrogenphosphate, and sodium phosphate were mixed in varying proportions, keeping the total analytical concentration of phosphate 0.2 mol/l. Another set of buffers was prepared using potassium dihydrogenphosphate, dipotassium hydrogenphosphate, potassium phosphate, and potassium chloride. In this series, buffers of pH 6.6, 7.6, 10.0, and 11.1 were prepared with the concentration of HPO_4^{2-} kept at 0.1 mol/l and ionic strength 0.5 mol/l. Borate buffers, pH 8–10, were prepared by titrating a solution of boric acid with sodium hydroxide keeping the total concentration of boric acid 0.2 mol/l. Potassium chloride was added to keep the ionic strength 0.5 mol/l. All solutions were purged with nitrogen for at least 2 min before recording the current–voltage curves.

Selection of Lignin Samples and Their Preparation

Preparation and properties of the enzymatically prepared lignins, which were used in the initial experiments, was described elsewhere[1–6].

The natural materials consisted of collected rotted wood which was passed though a screen with 0.114 cm openings before being washed with distilled water. The first natural material (P_1) was gathered from a rotten maple log. It was dried before grinding. An amount of 91 g of this material was dispersed in 1 l of distilled water for two days, filtered, and

dried. The second natural material (Q) was obtained from a rotten tree stump. One portion (Q) was used directly after grinding and screening. For a preparation of a second specimen (Q$_1$), 57 g of the natural material was dispersed for 4–55 days in 1 l of distilled water, filtered, and dried. The third natural material (R$_1$) was obtained from a rotted grey aspen log. After grinding and screening, 26 g of the powdery material was dispersed in 1.5 l of distilled water, filtered, and dried.

Four kraft lignins, Indulin ATR-CK1, RLX4290-2, PBI-M3A2801-28, and RLX4290-20A, all from Westvaco, Charleston Research Center, North Charleston (SC), were initially tested. The majority of the experiments were carried out with Indulin ATR-CK1 prepared from precipitated softwood kraft lignin and had the following characteristics: C$_9$ formula, $C_9H_{8.40}O_{2.39}S_{0.09}(OCH_3)_{0.79}$ (64.5% C, 5.82% H, 27.7% O, 1.6% S); unit weight 180; pH 3.68; ash 1.65%; acetone solubility 68.8%; carboxylic acid content 0.42 mol/kg. The surface area was about 100 m^2/g (BET). This material (177 g) was washed twice with 1.5 l of distilled water, dried (L$_1$), and sieved with a 120-opening/inch screen before use.

Procedures

Differential pulse polarographic (DPP) study of kinetics. To follow the reaction kinetics of the cleavage as a function of pH, 0.1 g of the studied material was suspended in 15 ml of the selected buffer in a polarographic cell. The buffer was purged with nitrogen for at least 2 min before the addition of the organic material and the DPP base line recorded. After the introduction of the organic material, the DPP curves were recorded at selected time intervals. Periodically some nitrogen was introduced to stir the solution. The current at infinite time was estimated and the natural logarithms of the difference between the peak current at infinite time and at a given time were plotted as a function of time. The rate constants at different pH values were obtained from the slopes of the linear portions of these plots.

Identification of reduction peaks. Appropriate amounts of lignin were dispersed in 0.2 M phosphate buffer of pH 11 and kept under nitrogen for 40 min. An aliquot was transferred to the electrolytic cell and a DPP curve recorded. Samples of vanillin, isovanillin, and syringaldehyde were added and increasing peaks were identified on the DPP curves.

Spectrophotometric study. An amount of 15 ml aliquots of a series of buffer were prepared in which 0.1 g of rotted wood or 0.02 g of indulin was dispersed. After varying time intervals, the reaction was quenched by adjusting the pH to 7.4 and the reaction mixture was filtered using a Millipore filter (0.45 μm). The sample was then transferred into a cell and spectra were recorded.

RESULTS AND DISCUSSION

Choice of Analytical Technique

Reactions occurring in buffered solutions containing suspended lignin were followed both by DPP and spectrophotometry. The use of chromatography necessitated the extraction of low-molecular-weight compounds from the reaction mixture before introducing the sample into an HPLC instrument. This approach was complicated by gel formation, resulting from the addi-

tion of the organic solvent to a sample containing cleavage products of lignin.

Comparison of absorption spectra (Fig. 2) and DPP curves (Fig. 3) indicates that the spectra do not manifest any characteristic adsorption maxima, only a gradual increase in absorbance with decreasing wavelength. Records obtained using DPP, on the other hand, show well developed peaks at about –1.6 V (SCE), which are attributed to hydroxy substituted aromatic aldehydes, and a less distinct peak between –1.2 and –1.3 V, in a potential range where α,β-unsaturated carbonyl compounds are reduced at pH 9–10. Polarographic curves further indicate the presence of compounds reduced at about –1.45 V, the nature of which has not been so far identified.

In pure aqueous solutions at pH 9–10, the three aldehydes which predominate among the products of cleavage of lignin, namely vanillin, 4-hydroxybenzaldehyde, and syringaldehyde, yield separated DPP peaks, but in the presence of surfactants in the reaction mixture, the peaks of these three aldehydes overlap. Hence the peak height is proportional to the sum of the concentrations of hydroxybenzaldehydes present. It is under-
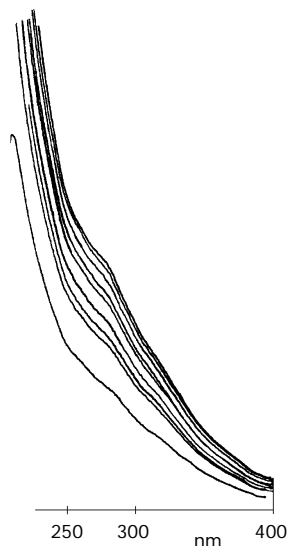

Fig. 2

Absorption spectra of hydrolysis products of 0.16 g grey birch lignin (R) in 25 ml phosphate buffer pH 9.8, μ = 0.5 as a function of time. Reaction stopped by addition of phosphoric acid to adjust the pH to 7.4 and the reaction mixture was filtered through a 0.45 μm Millipore filter. Time of quenching from the bottom (in min): 1, 3, 4, 5, 7.5, 10, 15, 25, and 60
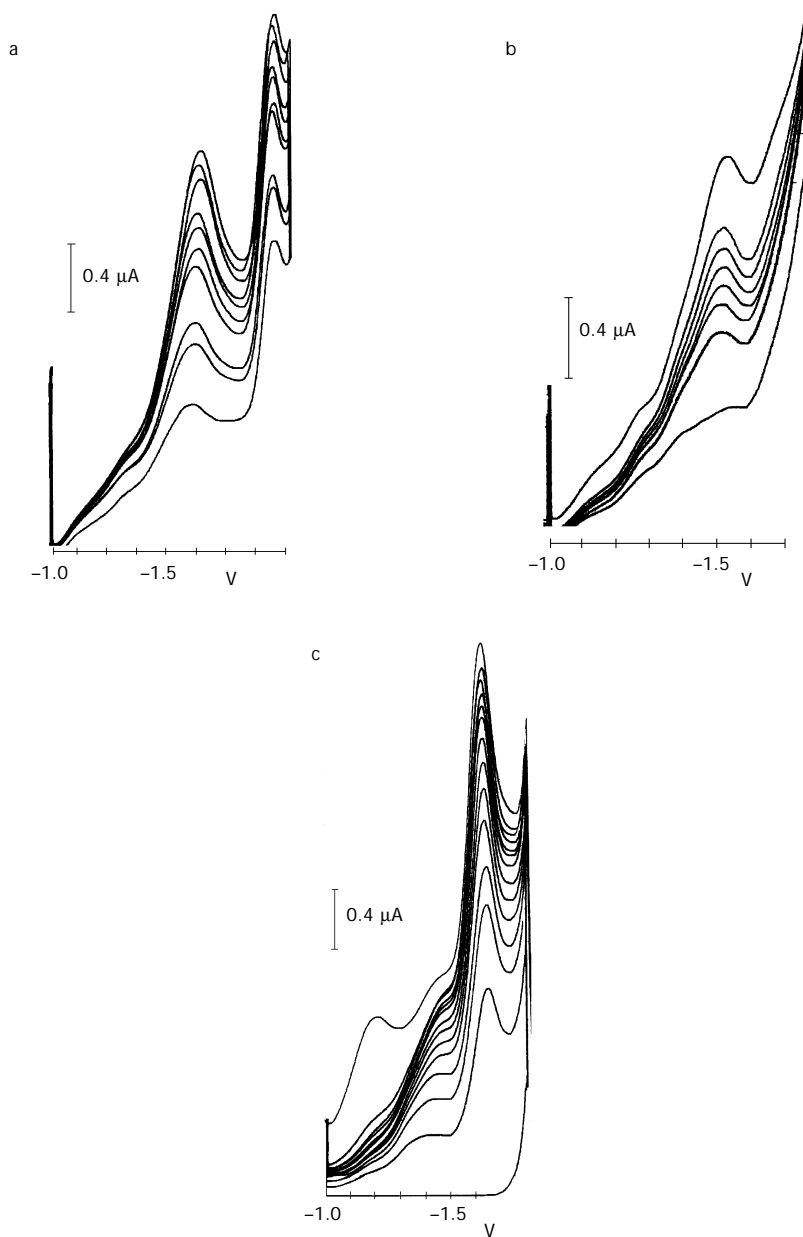
FIG. 3
Dependence of DPP current–voltage curves on time in a suspension of 0.1 g lignin in 15 ml of a phosphate buffer, pH 10.5: rot-wood lignin Q (a), rot-wood lignin P_1 (b), kraft lignin (c)

stood that in solutions containing surface-active compounds, limiting currents obtained in DC polarography or natural pulse polarography are less affected by surfactants than are peak currents obtained by DPP (ref.[11]). But for this particular problem, where the concentration of the surfactants during kinetic experiment remains unchanged and where only relative changes of peak current during the kinetic run are important for the evaluation, DPP was preferred because of the easier measurement of peak currents. The higher sensitivity of DPP was in this case not essential, as it was possible to achieve a convenient concentration range by adjusting the size of the sample.

Upon comparison of the change in absorbance at 250 nm with time with the change of the peak current at –1.6 V (Fig. 4), a similar pattern is indicated. As the absorbance at 250 nm is characteristic of all aromatic compounds, whereas the DPP peak at –1.6 V is only characteristic of aromatic aldehydes, it is indicated that either aromatic aldehydes are the predominant aromatic species in the reaction mixture, or that the various aromatic compounds resulting from the alkaline cleavage of lignin are formed in competitive reactions of the same order. With the possibility of choice, DPP was selected for further kinetic studies because the analysis can be carried out *in situ*, in real time. For spectrophotometry it is necessary to take samples from the reaction mixture, to quench the reaction by adjusting pH to 6
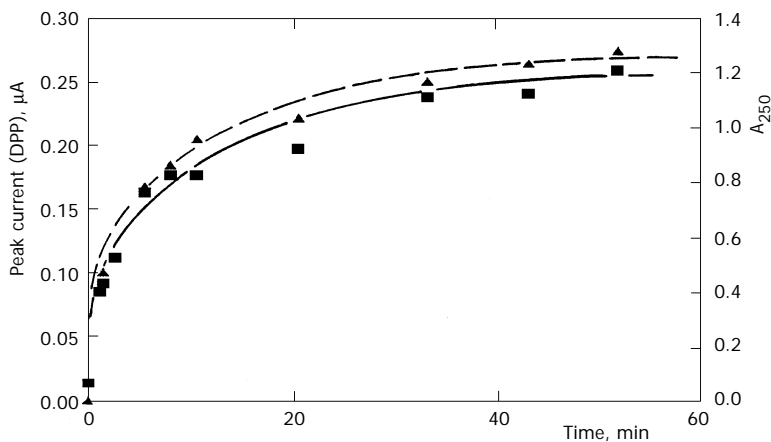

Fig. 4

Comparison of the time change of DPP current at –1.6 V (▲) with that of absorbance at 250 nm (■) in a suspension of 0.1 g lignin in 15 ml borate buffer, pH 10.0. Absorbance measured after quenching and ultrafiltration

or 7 and to remove solid particles by ultrafiltration. Moreover, the colloidal particles passing through the ultrafilter cause light scattering, which results in a large background.

For the above stated reasons, DPP was chosen and used in the following kinetic studies.

Kinetics of the Alkaline Cleavage of Lignin

The initial goal of the kinetic studies was to decide whether the alkaline cleavage of other studied samples of lignin follow a similar pattern as that of the natural, rot-wood lignin.

The pH range in which the cleavage was observed as well as the nature of species formed and the kinetics of the alkaline cleavage of samples of lignosulfonates, organosolv-lignins, periodate lignins, and expanded lignins, were completely different from those observed for rot-wood lignin. On the other hand, all microbiologically prepared lignins and, rather surprisingly, also the kraft lignins studied underwent at pH 9–10 similar cleavage resulting in the formation of hydroxybenzaldehydes. The time dependence of the concentration of these aldehydes followed a pattern similar to that observed for natural rot-wood lignins (Fig. 5). The change in concentration of hydroxybenzaldehydes, which is proportional to the peak
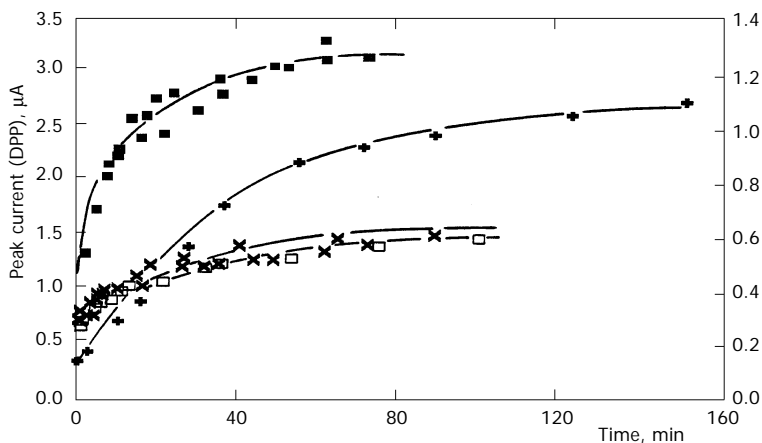

Fig. 5

Comparison of the change of the DPP current with time in the course of hydrolysis of 0.1 g of various lignins in 15 ml of borate buffer, $I = 0.5$, pH 9.0. Scale on the left for lignins Q and kraft, on the right for rot-wood lignins P_1 and R_1. Rot-wood lignin Q (■), rot-wood lignin P_1 (□), rot-wood lignin R_1 (×), kraft lignin (+)

current at –1.5 to –1.6 V, follows first-order kinetics as shown by the semilogarithmic plot (Fig. 6). The reproducibility of the time dependence of the peak current on sampling is demonstrated in Fig. 7, showing the kinetics in reaction mixtures obtained using two samples of the same lignin.
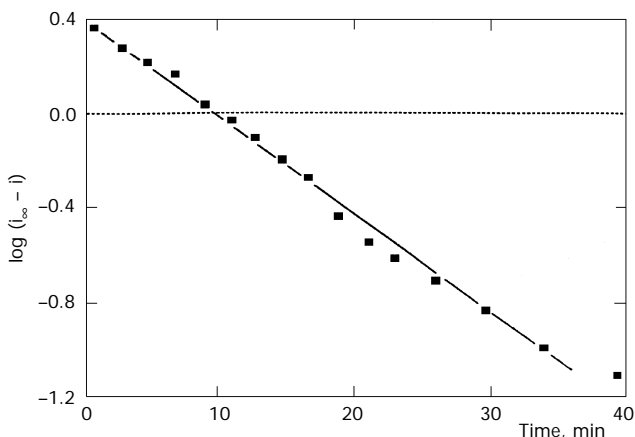

FIG. 6
First-order kinetic plots of log $(i_\infty - i) = f(t)$, where i_∞ and i are peak currents, for the hydrolysis of 0.1 g lignin Q in 15 ml of a borate buffer, pH 10.0
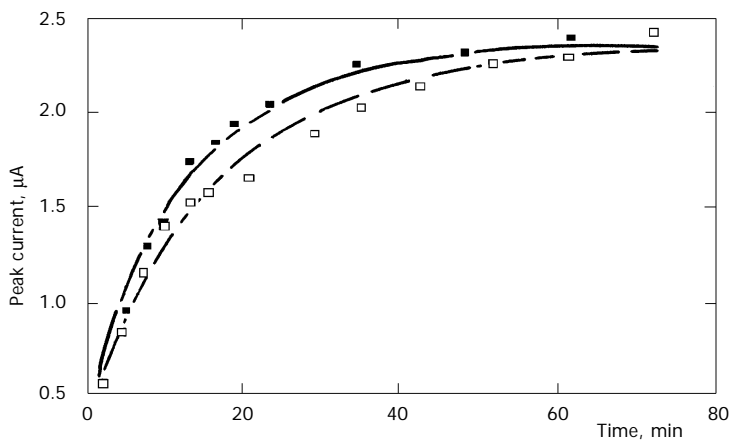

FIG. 7
Dependence of DPP peak current at –1.5 V on time in a suspension of 0.1 g of lignin Q in 15 ml of a borate buffer, pH 9.0, I = 0.5. Comparison of hydrolysis of two samples ■, ❑

The reaction rate increases with increasing pH and so does the concentration of the hydroxybenzaldehyde formed in the cleavage of the lignin polymer (Fig. 8). Only a part of the lignin is converted into soluble products. Gravimetry indicated that the conversion of the solid lignin particles into the water-soluble species increases with increasing pH from about 10% at pH 8 to about 20% at pH 11.5 (Table I). Using the plots of log $(i_\infty - i) = f(t)$, the first-order rate constants of the conversion were obtained at individual pH values. A plot of rate constants as a function of activity of hydroxide ions is non linear, but a plot against pH shows with increasing pH an in-

TABLE I
Percentage of lignin converted (0.3 g lignin (Q) in 10 ml of 0.1 M phosphate buffers). Reactions carried out at room temperature

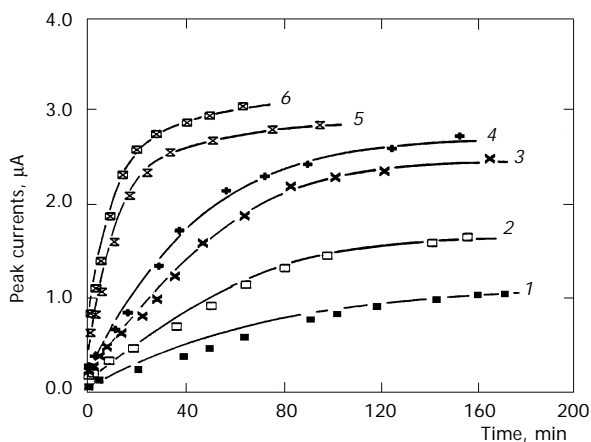| pH	Time of reaction	Weight loss, %
10.00	2 weeks	21
11.09	1.5 h	7.6–10
12.20	45 min	7.6–10
12.20	4 h	12.8–17.5

FIG. 8
Dependence of DPP peak current at –1.5 V on time in a suspensions of 0.1 g of rot-wood lignin Q in 15 ml of buffers of varying pH: 7.4 (*1*), 8.3 (*2*), 8.7 (*3*), 9.0 (*4*), 10.0 (*5*), 10.3 (*6*)

crease in the shape of a portion of a dissociation curve with pK_a about 11 (Fig. 9).

Mechanistic Considerations

As the measured rate constants are not a linear function of a_{OH^-}, it is possible to exclude that the rate-determining step in the cleavage of lignin is a nucleophilic attack of hydroxide ions either on carbonyl or on α,β-unsaturated carbonyl compounds. The observed dependence of the measured first-order rate constants on pH indicated that the rate-determining step of the cleavage of lignin is preceded by a rapidly established acid-base equilibrium. The conjugate base participates in the rate-determining step of the unzipping of the lignin polymer. The shape of the dependence of the measured rate constant on pH corresponds to an equation $k_{exp} = kK_a/(K_a + [H^+])$, where k_{exp} is the measured and k the intrinsic rate constant of the rate-determining step and K_a is the dissociation constant of the preceding acid-base reaction. The observed shape corresponds to a pK_a about 11, which is in the pK_a range of phenolic hydroxy groups. It is thus possible to assume that the unzipping of the polymer is initiated by a dissociation of some phenolic groups.
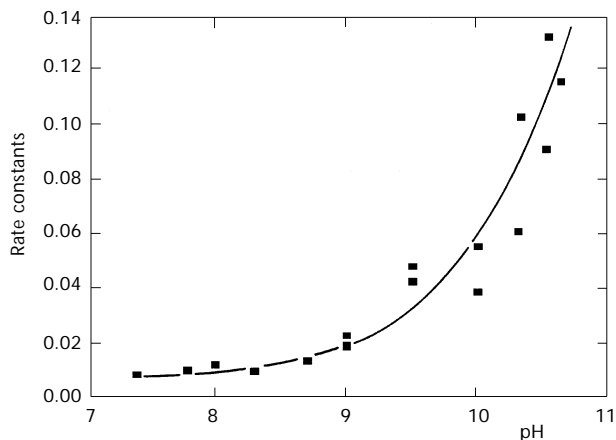

FIG. 9
Dependence of first-order rate constants on pH for the alkaline cleavage of kraft lignin in buffers

CONCLUSIONS

Polarography has been demonstrated to be well suited as an analytical method enabling following the kinetics of the alkaline cleavage of lignin. This is facilitated by placing the dropping mercury electrode into nonhomogeneous suspensions of lignin in buffered solutions. The concentration of hydroxybenzaldehydes is followed. Contrary to a rather generally accepted view, it has been demonstrated that even at 25 °C and at pH < 12, some 10–20% of lignin can be converted into small, soluble, reactive molecules which are promising as synthetic intermediates.

These studies also indicated that the electrochemical reductions and in particular oxidations, which have been carried out in alkaline solutions of lignin in Japan[12], Soviet Union[12–20], and Britain[21,22] did not involve the electrochemical conversion of lignin itself, but products of its alkaline cleavage. Among those which can undergo reduction or oxidation in alkaline media are in particular aromatic aldehydes, but possibly also products of the above-mentioned numerous consecutive reactions, which can occur in strongly alkaline media.

Under the mild conditions used, conversion of lignin is obviously not complete. It can be assumed that under the conditions used, the more strongly crosslinked parts of the polymer remain insoluble. But it should be pointed out that the goal of this study is not a complete cleavage of lignin, as preferred in the paper and cellulose industries, but to find conditions, under which simple mixtures of low-molecular-weight organic substances can be obtained. Particularly promising of such conversions under mild conditions for further exploration is the fact that these cleavages occur with sufficient rates and a usable degree of conversion even at atmospheric pressure and at 25 °C. This seems to be an energy-conserving approach to the future needs in syntheses of organic compounds.

REFERENCES

1. Kulik F., Wieber J., Pethica B., Zuman P.: *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *214*, 331.
2. Wieber J., Kulik F., Pethica B. A., Zuman P.: *Colloids Surf.* **1988**, *33*, 141.
3. Rubio M. A., Pethica B. A., Zuman P., Falkenhag S. I. in: *Dietary Fibers and Nutrition* (G. E. Ingelett and S. I. Falkenhag, Eds), p. 251. Academic Press, New York 1979.

4. Paden C. A., Frank A. S., Wieber J. M., Pethica B. A., Zuman P., Jurasek L.: *ACS Symp. Ser.* **1983**, *214* , 241.
5. Zuman P., Ainso S., Paden C., Pethica B. A.: *Colloids Surf.* **1988**, *33,* 121.
6. Ainso S., Paden C., Pethica B. A., Zuman P.: *Colloids Surf.* **1988**, *33,* 133.
7. Rupp E., Zhong Q., Zuman P.: *Electroanalysis (N. Y.)* **1992**, *4*, 11.
8. Rupp E. B., Zuman P., Šestáková I., Horák V.: *J. Agric. Food Chem.* **1992**, *40*, 2016.
9. Privman M., Rupp E. B., Zuman P.: *J Agric. Food Chem.* **1994**, *42*, 2946.
10. Ludvík J., Zuman P.: *Microchem. J.* **2000**, *64,* 15.
11. Rupp E., Zuman P.: *Anal. Lett.* **1994**, *27*, 939.
12. Yoshiyama A., Chen Ch. S., Tien L.-L., Nonaka T., Chou T.-Ch.: *Denki Kagaku* **1989**, *57*, 162; *Chem. Abstr.* **1989**, *110* , 194833.
13. Kovalenko E. I., Shifron E. M., Raskin M. N. in: *Novosti Elektrokhimii Organicheshikh Soedinenii* (L. G. Feoktistov, Ed.), p. 24. Zinatne, Riga 1973; *Chem. Abstr.* **1975**, *83*, 62159.
14. Kovalenko E. I., Smirnov V. A., Shalimov V. N.: *Zh. Prikl. Khim.* **1977**, *50*, 1741; *Chem. Abstr.* **1977**, *87*, 143300.
15. Erstgneev E. I.: *Zh. Prikl. Klim.* **1981**, *54*, 377; *Chem. Abstr.* **1981**, *94*, 193906.
16. Sergeev A. D., Zakazov A. N., Chupka E. I.: *Khim. Tehknol. Tsellyul.* **1981**, *8*, 25; *Chem. Abstr.* **1982**, *97*, 40519.
17. Stromskaya G. I., Martinova G. P., Chupka E. I.: *Zh. Prikl. Khim.* **1983**, *56*, 2539; *Chem. Abstr.* **1984**, *100*, 58708.
18. Kovalenko E. I., Raskin M. N., Smirnov V. A.: *Tr. Novocherk. Politekh. Inst.* **1976**, *320*, 69; *Chem. Abstr.* **1978**, *88*, 154596.
19. Stromskaya G. I., Martynova G. P.: *Deposited Doc.* **1982**, Viniti 1773; *Chem. Abstr.* **1983**, *98*, 162657.
20. Stromskaya G. I., Chupka E. I.: *Khim. Drev.* **1983**, 60; *Chem. Abstr.* **1983**, *98*, 81344.
21. Utley J. H. P. in: *Fundamental Thermochemical Biomass Conversion* (R. P. Overend, T. A. Milne and L. K. Mudge, Eds), p. 1087. Pap. Inf. Conf. Elsevier, London 1982 (Publ. 1985).
22. Utley J. P. H., Smith C. Z.: *PCT Int. Appl. WO* **1987**, *87* 03,014, 1987, p. 22; *Chem. Abstr.* **1988**, *109*, 8278.