MASTER

Electrochemistry Applied to Biomass

October 1980 — September 1981

Helena L. Chum, Editor

SERI

Solar Energy Research Institute
A Division of Midwest Research Institute

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NOTICE

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April 1982

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PREFACE

This report is the first in a series of progress reports to be issued for the task Electrochemistry applied to Biomass (Task No. 3356.50). This work is supported by DOE-BmES, with Dr. Carl Wallace as Technical Monitor.
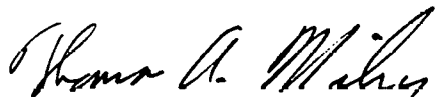
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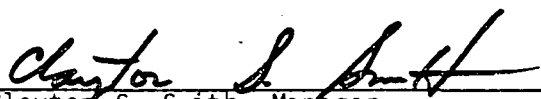
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ABSTRACT

This report addresses the research carried out during FY 1981 in the task Electrochemistry Applied to Biomass. This task investigates the electrochemical conversion of biomass-derived compounds, obtained through thermochemical pretreatments, into valuable organic chemicals, petrochemical substitutes, and energy-intensive chemicals.

A hardwood-derived lignin obtained from ethanol extraction of the explosively depressurized aspen has been investigated. We have partially characterized this lignin material, and have also submitted it to electrolyses under controlled potential. The electrolytic conditions employed so far affect mainly the carbonyl groups of the ethanol-extracted steam-exploded aspen lignin. We have some evidence of demethoxylation and changed phenolic content after electrolysis. During product isolation, fractionation of the lignin occurs. The material with decreased methoxyl content may be suitable to replace phenol in phenol-formaldehyde-type resins. We are continuing these electrochemical and chemical investigations. Gel-permeation chromatography is being used to separate and characterize the several lignin fractions. In addition, we are carrying out electrolyses under more powerful reducing conditions which may lead to the cleavage of the main bonds in the lignin molecule (the β-O-4 ether linkages) producing monomeric and dimeric phenolic compounds.

The electrochemistry and photoelectrochemistry of levulinic (4-oxo-pentanoic) acid, the major product of controlled degradation of cellulose by acids, have been investigated. This acid can be viewed as a major product of biomass thermochemical pretreatment or as a by-product of acid hydrolysis to fermentable sugars. Since this acid can be present in waste streams of biomass processing, we investigated the photoelectrochemical reactions of this acid on slurries composed of semiconductor/metal particles. The semiconductor investigated was undoped n-TiO_2, as anatase, anatase-rutile mixture, or rutile. In addition to the decarboxylation reaction leading to methylethylketone, we have also observed novel cleavages of the C-C backbone leading to propionic acid, acetic acid, acetone, and acetaldehyde as major products. The carboxylic acids formed undergo decarboxylation at the slurry diodes to ethane and methane. The electrochemistry of levulinic acid has been reviewed and some reactions have been experimentally confirmed and improved. We are addressing a novel synthetic reaction to dimerize the molecule of ethyl levulinate. The objective is to obtain 4,5-dimethyloctan-1,8-diol, which could be used to promote the solubility of lower alcohols in diesel fuel.

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SECTION 1.0

INTRODUCTION

The objective of this task is to convert, electrochemically, biomass or bio-mass-derived chemicals into valuable organic chemicals, petrochemical substi-tutes, and energy-intensive chemicals. The materials being investigated cur-rently are all obtained through the thermochemical pretreatment of biomass.

During the past year, the Electrochemistry Applied to Biomass task has con-centrated on the following projects: (a) the electrochemistry and chemical characterization of steam-exploded aspen lignin (Sec. 2.0); (b) the photoelec-trochemistry of levulinic acid on undoped platinized anatase powders (Sec. 3.0); and (c) the electrochemistry of levulinic acid and selected derived compounds (Sec. 4.0).

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SECTION 2.0

ELECTROCHEMISTRY AND CHEMICAL CHARACTERIZATION OF STEAM-EXPLODED ASPEN
(POPULUS TREMULOIDES) LIGNIN*

2.1 INTRODUCTION

By the early part of the 21st century chemicals derived from biomass will
probably be competitive in price with those obtained from petroleum. Except
when gasification or pyrolysis is employed, it will be essential to separate
and utilize fully each of the components of biomass; i.e., cellulose,
hemicelluloses, lignin, and extractives. Much of the technology for the
conversion of cellulose and hemicelluloses to chemical feedstocks has been or
is being developed, and the extractive materials will continue to be needed by
the fine chemicals industry. Lignin, however, has not been investigated fully
as a source of organic chemicals both because of its complex, irregular
structure and because of its value as a fuel to the pulp and paper industry.

An estimated 100 10^6 t/yr of hardwood is available in the United States
(Goldstein 1975). These woods are not used as heavily in the pulp and paper
industry as are softwoods except for applications that require short cellu-
losic fibers. Therefore, the hardwoods are an abundantly available form of
biomass, suitable for transformation into chemicals.

The steam explosion of hardwoods involves subjecting the biomass to saturated
steam at 3450-6900 kPa (500-1000 psi) for 5 seconds to 5 minutes at ~200°C
then reducing the pressure rapidly to atmospheric pressure. The biomass
explodes and becomes a powder. This pretreatment enables effective separation
of the cellulosic, hemicellulosic, and lignin fractions (Nguyen and
Noble 1981) by simple solvent extraction.

As part of the program on the electrochemistry of wood-derived products we are
studying a hardwood lignin (aspen, Populus tremuloides) extracted with ethanol
from wood that has been steam exploded. Work is underway currently to charac-
terize the aspen lignin and to evaluate electrochemical methods for either
transforming it into a more reactive but still polymeric form or for convert-
ing it into a mixture of monomeric and dimeric phenols.

2.2 RESULTS AND DISCUSSION

In a number of aspects the lignin extracted with ethanol from steam-exploded
aspen resembles that obtained by autohydrolysis (5 minutes or less) (Chua and
Wayman 1979). The lignins obtained after these treatments have similar IR and
UV-visible absorption spectra and comparable values for the methoxyl content
(Iotech Corp. 1979). The most noticeable of the dissimilarities is that the
number average molecular weight of the lignin extracted from the steam-
exploded wood is only half of that of autohydrolyzed aspen lignin. This

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*D.W. Sopher and H.A. Schroeder, Wood Sciences, Colorado State University, Fort
Collins, CO, and H. L. Chum.

comparison supports the suggestion (Allen et al. 1980) that explosive depressurization combines the chemical action of autohydrolysis with the mechanical action, which helps disrupt the lignin structure and prevents extensive repolymerization.

Based on the chemical and spectroscopic properties of the autohydrolyzed aspen lignin, Chua and Wayman (1979) concluded that one effect of the pretreatment is cleavage of the β-O-4 linkages followed by the formation of unconjugated ketone functions (Scheme 2.1):
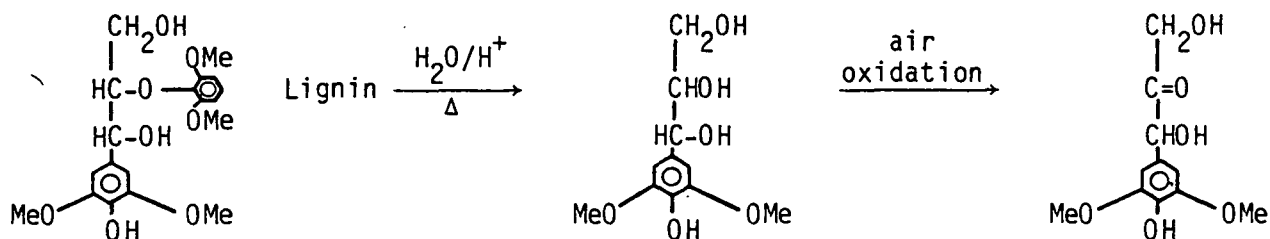
Scheme 2.1   Cleavage of β-O-4 Linkages Followed by Oxidation

Other probable autohydrolytic processes are the breaking of α-O-4 linkages and the cleavage of one of the methoxyl groups of the syringyl unit
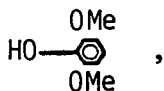
yielding guaiacyl units
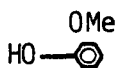
We conclude from our spectroscopic studies that similar processes occur during steam explosion. Additionally, we have established that a proportion (~20%-30%) of the p-hydroxybenzoate ester functions, which constitute up to 10% of the aspen lignin (Smith 1955), are hydrolyzed during the steam explosion process. The remaining ester groups are apparent in the IR spectrum of steam-exploded lignin that has been reduced with excess sodium borohydride.

Voltammetric studies of the ethanol-extracted aspen lignin at a hanging mercury drop electrode indicate that a number of electrochemical processes occur at low potentials, some faradaic and some probably due to adsorption. For comparison a number of other types of lignin were examined voltammetrically under the same conditions (Figs. 2-1 to 2-6). The exact form of the i-E curves obtained depends on the solvent, supporting electrolyte, and type of lignin (Table 2-1).

Controlled potential coulometry was used to determine that the peak observed during the voltammetry of aspen lignin in water/LiOH (Fig. 2-1) corresponded to only 1/30 F mol^{-1} for a $\overline{M}_w$ = 1000. The voltammetric behavior of lignin in MeOH/TBAP was examined up to -2.7 V (vs. Ag/AgCl). In addition to the low-potential processes, a shoulder at -2.55 V was observed (Fig. 2-6). At both platinum and vitreous carbon electrodes in DMF/LiClO$_4$, no clear voltammetric peaks or shoulders were observed up to -3.0 V vs. Ag/AgCl.
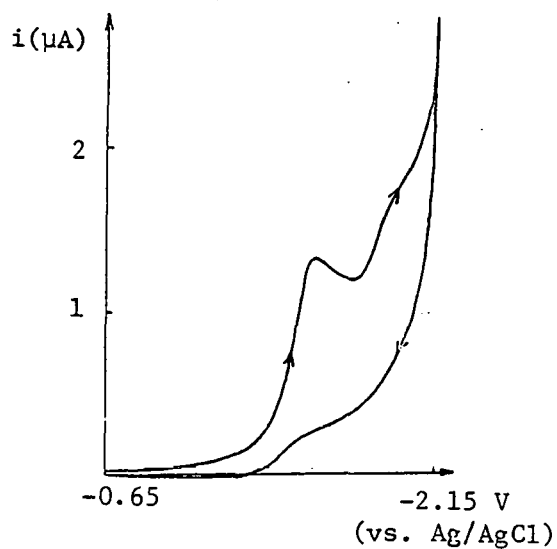
Figure 2-1. Cyclic Voltammogram of
Ethanol-Extracted,
Steam-Exploded Lignin
Aspen in Water/LiOH
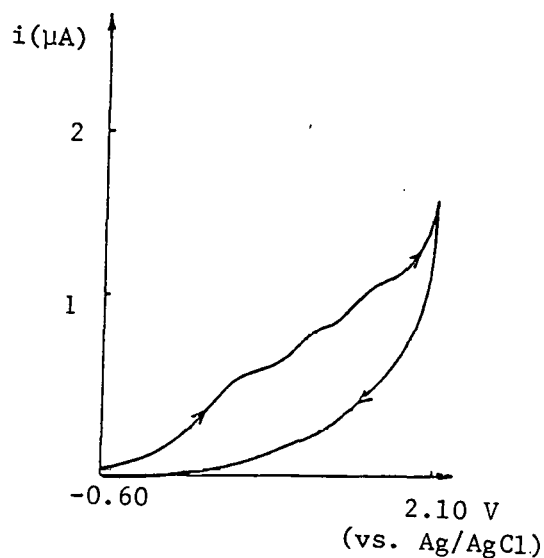
Figure 2-2. Cyclic Voltammogram of
Ethanol-Extracted,
Steam-Exploded Lignin
Aspen in Dimethyl-
formamide/Tetrabutyl-
ammonium Perchlorate
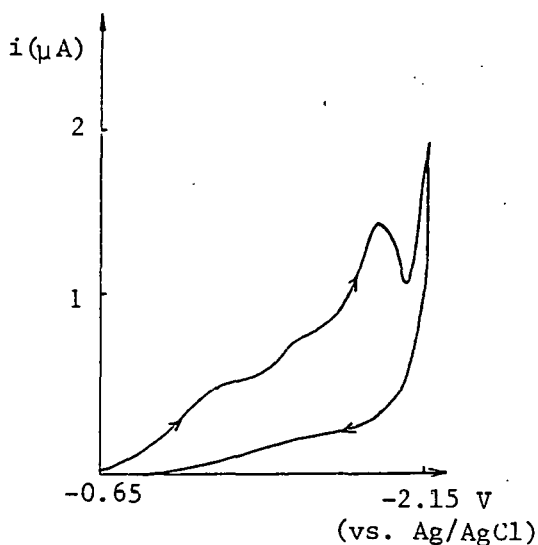
Figure 2-3. Cyclic Voltammogram of
Ethanol-Extracted,
Steam-Exploded Lignin
Aspen in Dimethyl-
formamide/$LiClO_4$
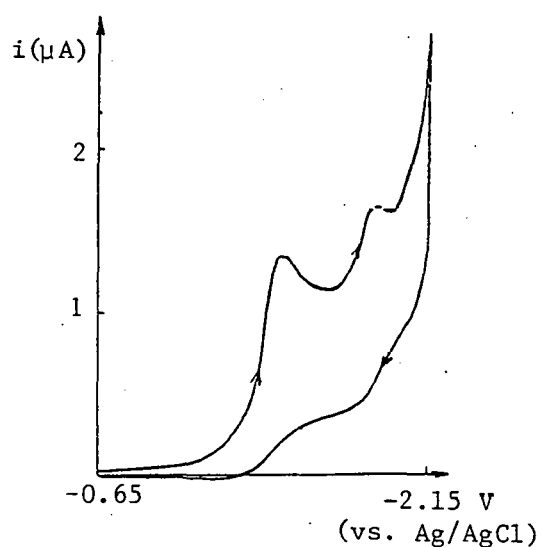
Figure 2-4. Cyclic Voltammogram of
Kraft Lignin (Low
Molecular Weight
Fraction) in Water/LiOH

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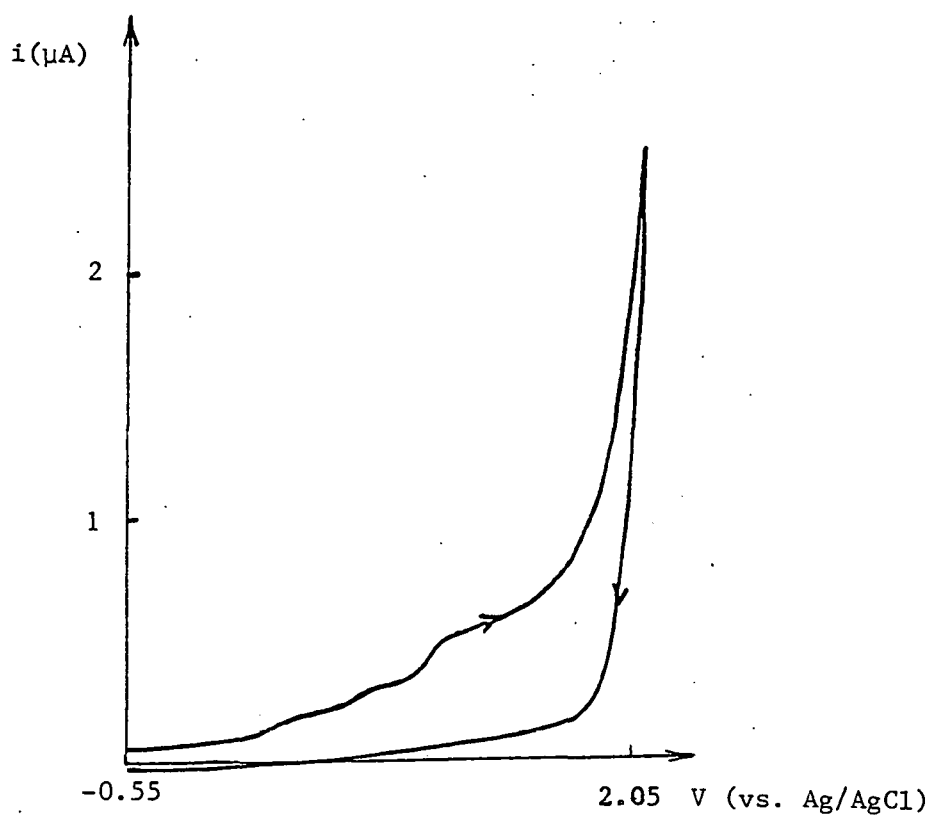
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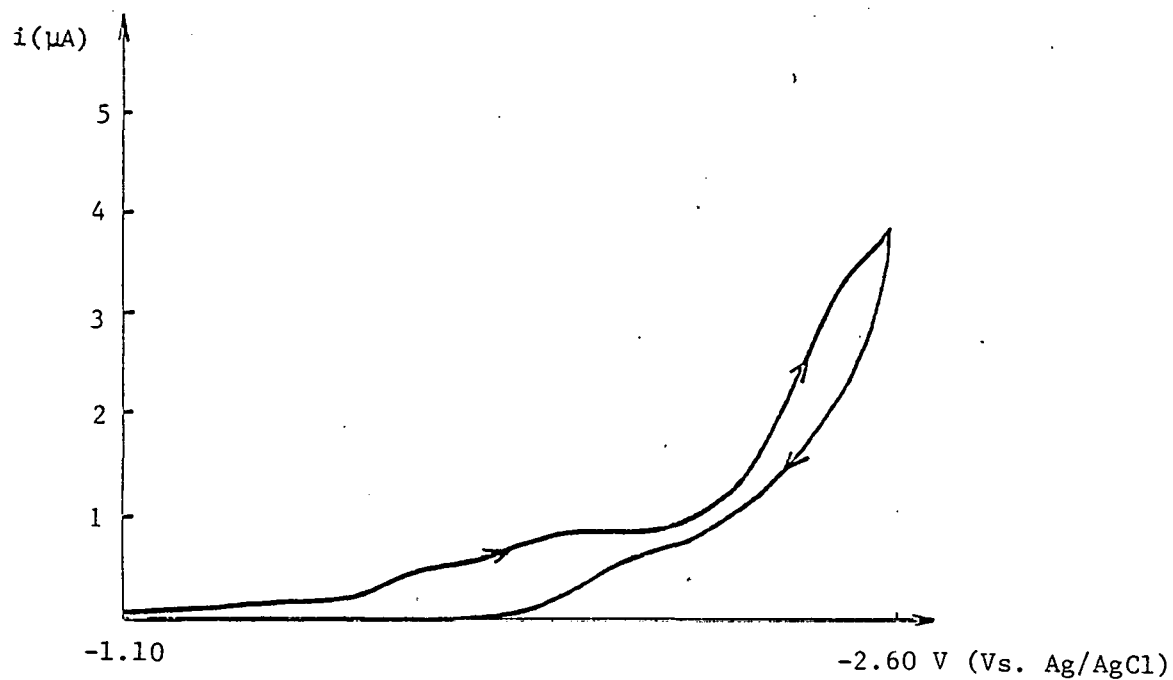
Figure 2-6. Cyclic Voltammogram of Ethanol-Extracted, Steam-Exploded Aspen
Lignin in Methanol/Tetraethylammomium Perchlorate

Table 2-1. Voltammetric Results (in Volts ±0.05 V vs. Ag/AgCl) for Various Types of Lignin

Lignin	Supporting Electrolyte/Solvent		
	LiOH/H$_2$O	LiClO$_4$/DMF	TBAP/DMF
Ethanol-extracted exploded aspen	-1.54(pk),-1.80(s)	-1.20(s),-1.50(s),-1.84(pk)	-1.20(s),-1.60(s),-1.80(s)
Lignosite (Ca^{2+})	-1.50(s),-1.75(s)	-1.15(s),-1.40(s),-1.60(s)	-1.20(s),-1.70(s)
Kraft lignin	-1.45(pk),-1.85(s)	-1.75(s)	-1.85(s)

Notes: s = shoulder
     pk = peak.

A number of controlled-potential electrolyses and alkali metal amalgam reductions have been carried out on aspen lignin. The results are summarized in Tables 2-2 and 2-3. The IR and UV spectra of the products isolated from the electrolyses at -2.0 V indicate that reduction of both conjugated and unconjugated ketones occurred. The conjugated ketones are probably of the type shown schematically as Compound 1. Such functions would be readily reduced electrochemically and may account for the lower potential faradaic processes observed in voltammetry. Simple unconjugated ketones such as benzylmethyl ketone (Compound 2) are reduced at potentials 0.3 to 0.5 V more cathodic than the potential employed in these reductions (Powers and Day 1959). However, the presence of α-hydroxy groups lowers the reduction potential to ca. -1.9 V vs. SCE (Fedoronko 1966). It is likely that most β-keto functions in lignin are adjacent to a hydroxyl group. Therefore, we conclude that α-hydroxy keto functions (shown schematically as Compound 3) are being reduced in the electrolyses at -2.0 V. Another possibility is that $\alpha\beta$ unsaturated carbonyl functions are reduced under these conditions.
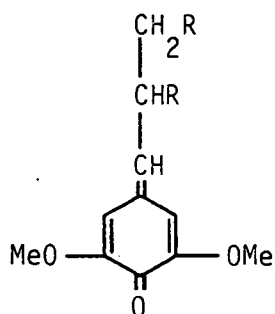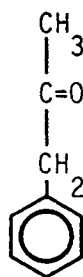
Compound 1   Compound 2   Compound 3
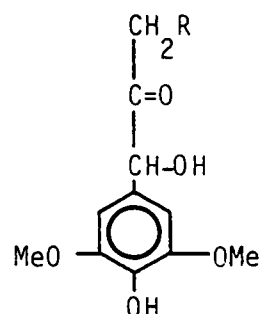
The reactions of lignin with lithium and sodium amalgams proceeded very slowly. When lignin was stirred for 60 hours with an excess of lithium amalgam, prepared electrochemically in $DMF/LiClO_4$, only limited reduction occurred (see Table 2-3). Sodium amalgam, generated in water/NaOH and reacted with lignin for 60 hours, brought about a similar degree of reduction.

The electrolysis of lignin in methanol/TBAP at -2.7 V (vs. Ag/AgCl), using a mercury cathode, resulted in the total reduction of not only α-hydroxyketo groups but also α,β-unsaturated carbonyl functions. Extensive reduction was also observed when lignin was electrolyzed in DMF/TBAP at -2.6 V (vs. Ag/AgCl), with a mercury cathode.

A number of lignin samples and electrolysis products have been analyzed for methoxyl content. The results obtained, which reflect the severity of the pretreatment and extraction procedures, are given in Table 2-4. By our method the lignin extracted with ethanol appears to have a higher methoxyl content than that extracted with 0.1 M NaOH. Lignin samples obtained from aspen which has been steam exploded under conditions to optimize lignin extraction have a lower methoxyl content. The lignin reduced in water/LiOH and $DMF/LiClO_4$ had fewer methoxyl groups than the original material. Whether a concomitant increase in phenolic hydroxyl content occurs during the electrolysis is yet to be established by analyses to be carried out at Colorado State University (chemical studies) and SERI (conductiometric studies).

Table 2-2. Preparative-Scale Electrolysis of Ethanol-Extracted, Steam-Exploded Aspen: Relative Intensity of the IR Spectra at ν_{1710} and ν_{1515}

Conditions	Extent of Electrolysis (Faradays/mole[a])		Relative Intensity (ν_{1710}/ν_{1515})	
Ethanol-extracted aspen lignin	0		0.85-0.90	
DMF/TBAP/Hg at -2.0 V[d]	2.5	0.62[b]		0.40[c]
DMF/LiClO$_4$/Hg at -2.0 V[d]	2.3	0.62[b]		0.53[c]
EtOH/water/NaBH$_4$	excess		0.43	

[a] $\overline{M}_w$ is assumed to be 1000.

[b] Material precipitated from the catholyte reaction mixture after addition of 0.5 M HCl.

[c] Material soluble under conditions described in (b) but extracted with ethyl acetate.

[d] Versus Ag/AgCl.

Note: ν 1710 cm^{-1} is the C=O stretching frequency.
        ν 1515 cm^{-1} is an aromatic C-C stretching frequency.

Table 2-3. Preparative-Scale Electrolysis of Ethanol-Extracted, Steam-Exploded Aspen: Relative Intensity of the IR Spectra at ν_{1710} and ν_{1515}

Conditions	Extent of Electrolysis (Faradays/mole[a])		Relative Intensity (ν_{1710}/ν_{1515})	
Ethanol-extracted aspen lignin	0		0.85-0.90	
DMF/LiClO$_4$/Li(Hg)	9	0.62[b]		0.64[c]
H$_2$O/NaOH/Na(Hg)	14	0.62[b]		---
MeOH/TBAP/Hg at -2.7 V[d]	6	0.44[b]		0.36[c]
DMF/TBAP/Hg at -2.6 V[d]	3	0.57[b]		0.48[c]
Ethanol/NaBH$_4$ (excess)	--		0.43	

[a]$\overline{M}_w$ is assumed to be 1000.

[b]Material precipitated from the catholyte by the addition of 0.5 M HCl.

[c]Material soluble under conditions described in (b) but extracted with ethyl acetate.

[d]Versus Ag/AgCl.

Note: ν = 1710 cm^{-1} is the C=O stretching frequency.
ν = 1515 cm^{-1} is an aromatic C-C stretching frequency.

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We propose in the near future to investigate the vigorous reduction of aspen lignin by using tetraalkyl ammonium amalgams and solvated electrons. Under such strong reducing conditions we believe that ether functions in the lignin, including methoxyl groups, may be cleaved (Horner and Neumann 1965; Pernelmam and Dence 1974).

Table 2-4. Analysis of Lignin Samples for Methoxyl Content

Lignin Sample	% Methoxyl
Ethanol-extracted exploded aspen	15.3
Aqueous-NaOH extracted exploded aspen	12.7
Ethanol-extracted aspen--steam explosion process optimized for lignin extraction	12.7
Ethanol-extracted aspen--reduced in $H_2O/LiOH$ (-2.0 V[a])	12.3
Ethanol-extracted aspen--reduced in $DMF/LiClO_4$ (-2.0 V[a])	11.1
High $\overline{M}_w$ Kraft (Westvaco)	9.6
Low $\overline{M}_w$ Kraft (Westvaco)	13.2

[a]Versus Ag/AgCl.

2.3 EXPERIMENTAL SECTION

Infrared absorption spectra (Nujol mulls) were recorded by a Perkin Elmer 599B and ultraviolet absorption spectra (ethanol solutions) were obtained using a Hewlett Packard 8450A.

Methoxyl content was measured in the Department of Forest and Wood Science at CSU by reacting the lignin with hydroiodic acid and determining the methyl iodide formed (Browning 1967).

Polarograms and voltammograms at hanging mercury drop were recorded using a PAR 303 Mercury Electrode and a PAR 174A Polarographic Analyzer. Voltammograms at platinum and vitreous carbon were obtained using a PAR 173 Potentiostat in conjunction with a PAR 175 Universal Programmer.

For controlled potential electrolyses one of two potentiostats was used: either a Bioanalytical Systems SP2 or a Wenking HP 72. To measure the charge consumed a digital coulometer was employed (ESC 640). All lignin reductions were carried out in a glass cell with a stirred mercury pool cathode (area $\approx$ 16 cm^2). The secondary electrode (platinum disc; area $\approx$ 12 cm^2) was parallel to the working electrode and separated from the catholyte by a sintered glass disc.

The following is a description of a representative electrolysis of lignin and product isolation procedure. Lignin (1.0 g, ~10^{-3} mol) was dissolved in 10 cm^3 of electrolyte (0.2 mol dm^{-3} Bu_4NClO_4 in DMF) and added to the cathode compartment (total solution volume ~50 cm^3). After degassing the cell with

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nitrogen, the lignin was reduced at -2.6 V (vs. Ag/AgCl) for ~3 F mol^{-1}. Towards the end of the electrolysis the color of the catholyte, originally dark brown, became yellow. To isolate the products the catholyte was added to degassed dilute hydrochloric acid (100 cm^3, 0.5 mol dm^{-3}). A pale brown precipitate and a globule of dark brown oil formed. After stirring the mixture for 30 minutes at 0° the oil solidified and broke up to give a light brown suspension. The solid material was separated from the solution by centrifugation (10,000 rpm, 30 minutes). The supernatant liquid was retained and the solid material washed with water (2 x 250 cm^3) followed by drying in a vacuum dessicator. Infrared analysis showed that the light brown powder (0.90 g) was a mixture of lignin and supporting electrolyte. By stirring the product in degassed water at 60° the Bu$_4$NClO$_4$ was dissolved, leaving the lignin which was filtered and dried (light brown solid, 0.67 g).

To isolate the lignin remaining in the supernatant liquid, the solution was saturated with potassium chloride and extracted with ethyl acetate (4 x 30 cm^3). The combined extracts were washed with water (4 x 50 cm^3), dried (MgSO$_4$), and the solvent evaporated under reduced pressure to give a viscous brown oil. Residual DMF was removed by high vacuum distillation and the remaining waxy solid was induced to solidify by the addition of water (5 cm^3). The lignin was dissolved from the solid by adding a few drops of concentrated sodium hydroxide solution and was filtered free of the supporting electrolyte. To reprecipitate the lignin a few drops of concentrated hydrochloric acid were added to the solution. The lignin was filtered off and dried to give a brown powder (0.15 g).

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SECTION 3.0

PHOTOELECTROCHEMISTRY OF LEVULINIC ACID ON UNDOPED PLATINIZED n-TiO$_2$ POWDERS*

3.1 INTRODUCTION

Photoelectrochemical systems utilizing various semiconducting materials are currently of interest principally in electrochemical systems that can utilize sunlight (0.9 to 3.2 eV per photon) for the production of electrical energy or to produce useful chemicals. Recent reviews of the field of photoelectrochemistry have been published (e.g., Bard 1979 and 1980; Nozik 1978 and 1981; Wrighton 1979).

Photoelectrosynthetic systems that consist of microscopic particles of semiconductor powders suspended in the solution of the reactive substrate are potentially a very simple approach to carry out photoelectrocatalytic or synthetic reactions. The most efficient particulate systems are heterogeneous and consist of the semiconductor material (n- or p-type) in contact with a metal. A variation includes a diode containing n- and p-types of semiconductors. The first type of heterogeneous systems, semiconductor/metal particles, has been successfully prepared by in situ photoreduction of metal ions onto the doped or undoped semiconductor (e.g., TiO$_2$, WO$_3$) particles by Reiche et al. (1979). The energetics of these heterogeneous structures result in the most efficient system for the spatial separation of photogenerated electrons and holes; electrons are easily removed from the metal, while holes are easily removed from the n-type region to drive reduction and oxidation reactions, respectively, in the substrate solution (Nozik 1981).

The following are examples of the application of homogeneous nonmetallized semiconductor powder reactions. Iron-doped rutile powders have been shown to reduce nitrogen to ammonia and smaller amounts of hydrazine (Schrauzer and Guth 1977). Cyanide is photocatalytically oxidized to mainly CNO⁻ at TiO$_2$, SnO$_2$ and CdS powders, whereas sulfite ions are photooxidized to sulfate ions at these powders and also at Fe$_2$O$_3$ (Frank and Bard 1977). A variety of semiconductor powders (SiC, GaP, CdS, TiO$_2$, SnO, WO$_3$) were shown to reduce carbon dioxide to mixtures of formic acid, formaldehyde, and methanol, with the first three semiconductor materials producing higher yields of methanol (Inoue et al. 1977). Strontium titanate powders were shown to photoreduce carbon dioxide to methanol and traces of formaldehyde (Aurian-Blayeni et al. 1980).

Examples of reactions of heterogeneous semiconductor/metal photochemical diodes include nitrogen reduction to ammonia by using a single crystal p-GaP/Al system (Dickson and Nozik 1978), decarboxylation of carboxylic acids

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*H.L. Chum, M. Ratcliff, F.L. Posey, with the cooperation of J.A. Turner and A.J. Nozik from the SERI Photoconversion Branch.

(Kraeutler and Bard 1978 and 1978a; Izumi et al. 1981) on platinized doped and undoped n-TiO$_2$ (anatase and rutile) and water splitting extensively reviewed in references in the first paragraph of this section. Methane was observed as reduction product of carbon dioxide on Pt/SrTiO$_3$(III) (Hemminger et al. 1978). St. John et al. (1981) have shown that upon irradiation of glucose solutions containing platinized doped anatase powders hydrogen and carbon dioxide are formed. These results are similar to those obtained by Kawai and Sakata (1980) with ternary powder systems RuO$_2$/TiO$_2$/Pt on starch, cellulose, and sucrose. No attempt has been made to elucidate the composition of the solutions after irradiation.

In 1978, Kraeutler and Bard described a new Kolbe (see Utley 1974) reaction pathway, obtained when acetate solutions are irradiated in the presence of particulate photoelectrochemical diodes of n-TiO$_2$/Pt. The major product of that reaction was methane; ca. 10% of ethane, the Kolbe product, along with some hydrogen were also detected. Experiments with deuterated water yielded CH$_3$D as the major product, consistent with a reduction reaction involving the solvent water, and no hydrogen abstraction from the acetic acid methyl groups. The platinized semiconductor particles act as short-circuited electrodes. Illumination with light of energy greater than the bandgap (>3-3.2 eV) of the semiconductor causes the formation of electron-hole pairs. The recombination of the electron-hole pairs is partially prevented by the following fast chemical reactions. The holes oxidize acetate ions to CH$_3$CO$_2$· radicals, which rapidly decompose to methyl radicals and carbon dioxide. The electrons reduce protons of the solvent to hydrogen. The by-product hydrogen and the isotopic substitution pattern indicate that the methane formed is a result of the reaction between methyl radicals and hydrogen (from the solvent).

Kraeutler and Bard (1978a) extended this investigation to other saturated carboxylic acids, namely, propionic, butyric, valeric, pivalic, adamantane-1-carboxylic. All of these acids were photoelectrochemically decarboxylated to the corresponding hydrocarbons. The influence of solution composition, reaction temperature, light intensity, and semiconductor properties (crystallographic structure and doping) were investigated in detail for the acetic acid/acetate system. The optimum pH for the decarboxylation was found to be ~3.5, with one-half to one-third of that rate being found in the more acid (pH ~1) and neutral to more alkaline regions (pH ~6-8). The anatase powders were found to be more reactive than the rutile particles. The reactivity for anatase increased in the following order: undoped < doped < undoped, platinized < doped, platinized. The rate is decreased by decreasing the light intensity (from 1600 W to 450 W) and temperature (from 55° to 45°C). The decarboxylation rate was found to be a function of carboxylate concentration only at low concentrations of carboxylate ions. This finding suggested adsorption of the carboxylate anions or acids as an important step.

The mechanism proposed by Bard et al. (1978a) for the reaction was the following (see also Scheme 3.1):

(1) excitation of electrons from valence band to the conduction band by light of energy greater than the semiconductor band gap.

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

$$P_T$$

$$(RCO_2H)_{ADS} \longrightarrow (RCO_2^-)_{ADS} + (H\cdot)_{ADS}$$

$$n\text{-}TiO_2$$

$$\frac{h\nu}{E \geq E_G}$$

$$e^-$$

$$h^+$$

$$e^-$$

$$RH$$

$$(RCO_2^-)_{ADS} \longrightarrow (RCO_2\cdot)_{ADS} \longrightarrow (R\cdot)_{ADS} + CO_2$$

SCHEME 3.1

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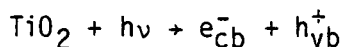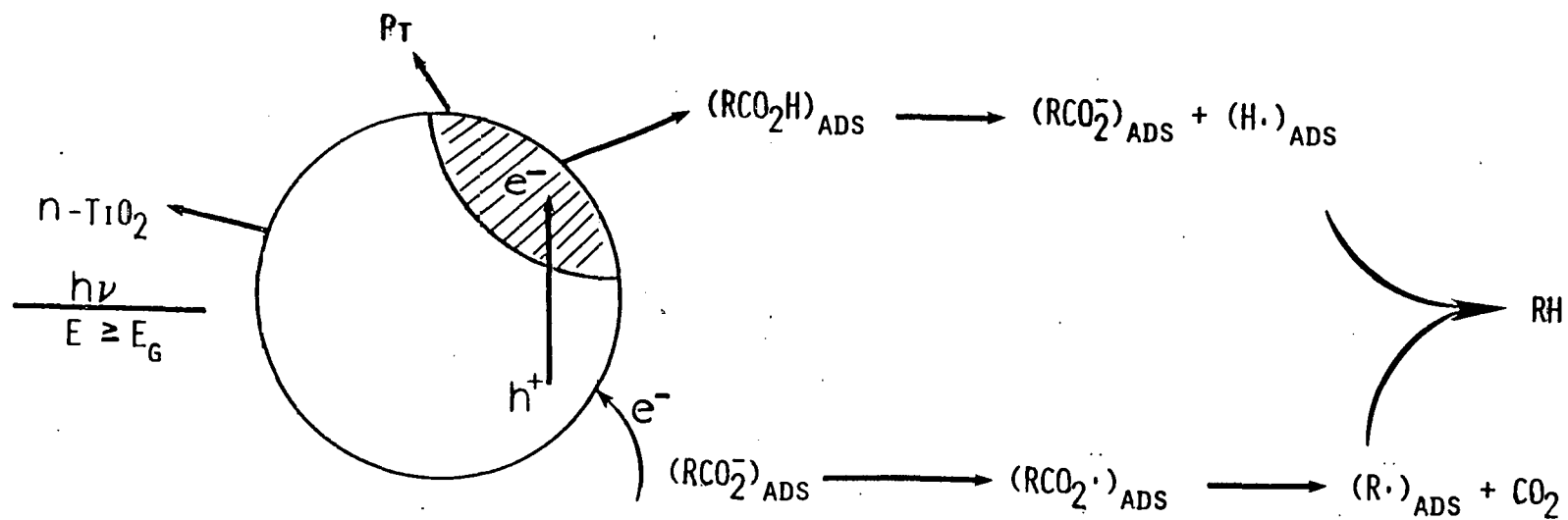
(2) band bending at the interface; the electric field in the space charge region will promote the separation of electrons and holes.

This makes possible the trapping of the separated charges at the surface:

$$e_{cb}^- \rightarrow e_{tr}^-$$
$$h_{vb}^+ \rightarrow h_{tr}^+$$
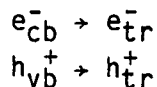
(3) The trapped holes can oxidize carboxylate ions or water:

$$h_{tr}^+ + RCO_{2ads}^- \rightarrow R\cdot + CO_2$$
$$h_{tr}^+ + H_2O_{ads} \rightarrow HO\cdot + H^+$$
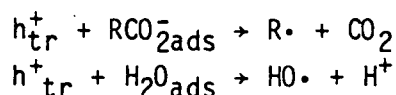
(4) The trapped electrons can perform reduction reactions, e.g.:

$$e_{tr}^- + RCO_2H \rightarrow H_{ads} + RCO_2^-$$
$$e^- + R\cdot + RCO_2H \rightarrow RH + RCO_2^-$$
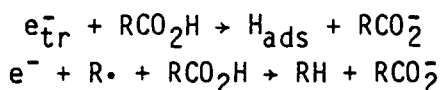
(5) By-products result from radical recombination reactions:

$$2R\cdot \rightarrow R_2$$
$$2H_{ads} \rightarrow H_2$$
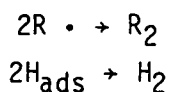
Kraeutler, Jaeger, and Bard (1978) observed directly the participation of radical intermediates through electron spin resonance. The methyl radicals were reacted with α-phenyl-n-tert-butylnitrone, and the adduct gave the expected spectrum. Direct radical detection was made in the case of triphenyl acetic acid, in which the triphenyl methyl radical was observed.

The photodecarboxylation of adipic acid led to butane. The intermediate, valeric acid, was also observed (Izumi et al. 1981).

Kraeutler and Bard (1978a) suggested that these reactions could be used to treat waste streams of saturated carboxylic acids. In such streams, principally those derived from biomass, polyfunctional carboxylic acids can be present. At SERI we started the systematic investigation of the photoelectrochemical reactions involving a simple polyfunctional carboxylic acid, namely, 4-oxopentanoic (levulinic) acid on platinized undoped n-TiO$_2$ particulte systems. Partial results have been reported in the literature (Chum et al. 1981) and the full paper is forthcoming.

3.2 RESULTS AND DISCUSSION

The influence of levulinic acid concentration, pH, crystallographic phase of n-TiO$_2$, and level of metallization of the semiconductor on the rate of decarboxylation of levulinic acid and on the organic volatile product distribution have been investigated.

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3.2.1 Rate of Carbon Dioxide Evolution

The rate of carbon dioxide formation at 55°-65°C, at pH 2-7, in the presence or absence of metallized n-TiO_2 powders, but in the absence of illumination is 0-0.5 μmole/h. In the absence of the powders, but under illumination a rate of carbon dioxide evolution of about twice that value was observed. A clear yellow solution resulted after prolonged illumination. Upon illumination of suspensions of platinized or unplatinized undoped n-TiO_2 as anatase, or a mixture of anatase and rutile, or rutile, appreciable evolution of carbon dioxide occurs, 10-150 times faster than the thermal or photoblank experiments. The rates depend on the crystallographic phase of n-TiO_2, level of platinization of the semiconductor, pH, and levulinic acid concentration as shown in Figs. 3-1 and 3-2.

The rate of carbon dioxide evolution decreases slightly as the concentration of acid decreased from 4 to 2 M (see Fig. 3-1). The decrease is more pronounced at lower concentrations. The rates of carbon dioxide evolution on unplatinized anatase and mixtures of anatase:rutile (70:30%) are comparable (cf., experiments 22 & 37) in 2 M levulinic acid. For the platinized powders, the rate of CO_2 evolution of the anatase:rutile mixture is somewhat larger than that of anatase (cf. experiments 28, 15, and 36). Both anatase and anatase-rutile mixtures have 5-8 times larger decarboxylation rates than the pure rutile phase of n-TiO_2.

The effect of pH on the rate of decarboxylation is shown in Fig. 3-2. The data were obtained at 2 or 4 M levulinic acid. The Pt loading of the semiconductor powders used in these experiments ranged from 1%-5%. A pH dependence similar to that obtained by Kraeutler and Bard (1978a) for acetic acid is observed for levulinic acid, with a maximum rate at pH ~4.

At pH = 3.5 experiments were performed with slurries containing less than 1% platinum loading. At 1% the rate of decarboxylation is ~80 μmol/h. At 0.2%, the rate of decarboxylation decreases to 55 μmol/h; with a loading of 0.04%, the rate decreased to 45 μmol/h, approaching the behavior of the nonmetallized powder. Platinum loadings of 1%-5% seem to be sufficient to give reasonably reproducible carbon dioxide evolution rate data.

3.2.2 Organic Product Distribution

The expected product of the photoelectrochemical decarboxylation of levulinic acid on n-TiO_2 powders is methylethylketone if a reaction similar to that observed by Kraeutler and Bard (1978) for aliphatic carboxylic acids occurs:

$$H_3C\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_2H_4\text{-}CO_2H \xrightarrow[\text{n-}TiO_2/Pt]{h\nu} H_3C\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_2H_5 + CO_2 \qquad (3\text{-}1)$$
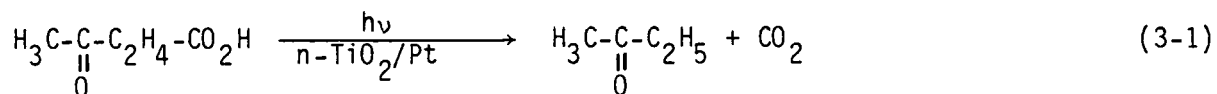
Indeed, this ketone was identified as one of the organic reaction products in all experiments performed with levulinic acid and n-TiO_2. However, in addition to this expected product, several volatile organic compounds were
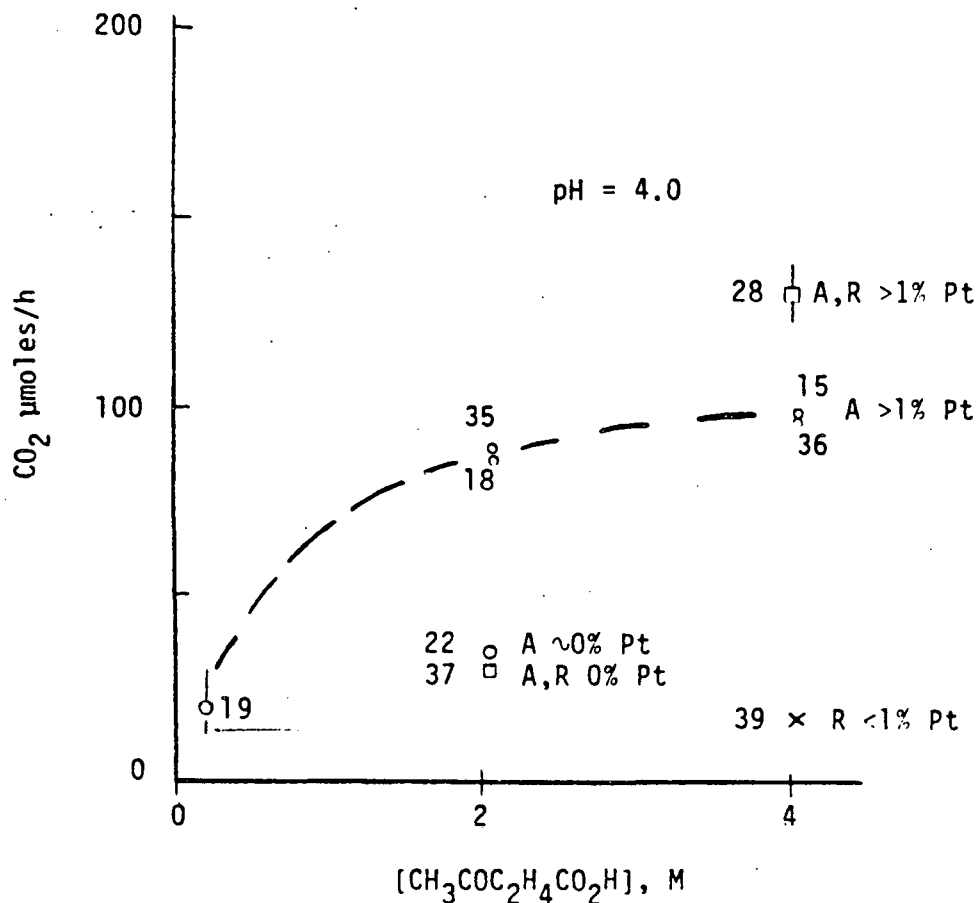
Figure 3-1. Dependence of the Rate of Catalytic Photoelectrochemical Formation of Carbon Dioxide on the Concentration of Levulinic Acid at pH = 4.0, on Undoped Platinized (1-5 wt % Pt) Anatase [A > 1% Pt] (5 mg Pt/TiO_2/ml solution) [Experiments 19, 18, 35, 15, 36]. Effect of the crystallographic phase and level of platinization also shown at various concentrations of levulinic acid. A, R = 70:30 wt % anatase, rutile; R = rutile. Levels of platinization indicated in the figure. Temperature = 65°C, pH = 4.0; no oxygen present.

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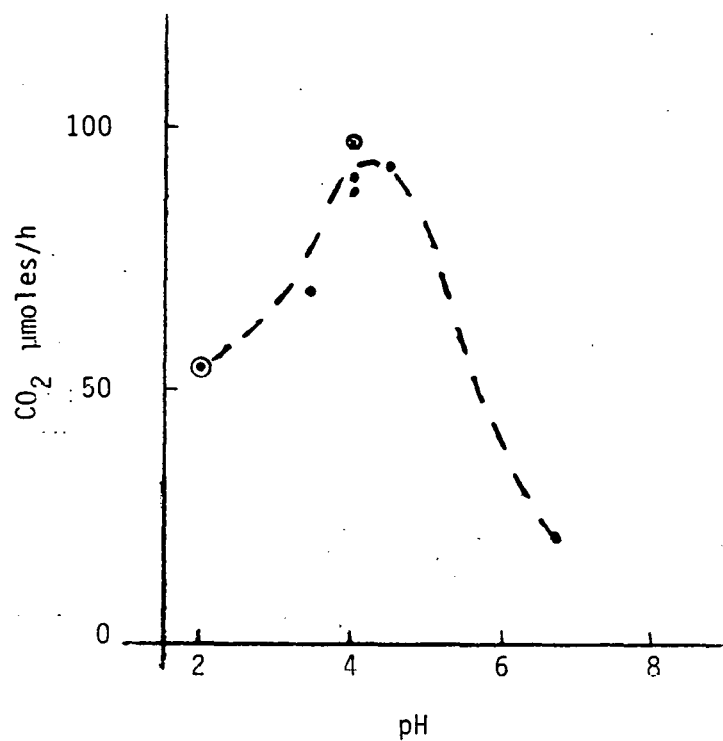
Figure 3-2. pH Dependence of the Rate of Catalytic Photoelectrochemical Formation of Carbon Dioxide from Levulinic Acid on Undoped Platinized (1-5 wt % Pt) Anatase (5 mg Pt/TiO$_2$/ml solution) at 65°C

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identified by GC-MS: methanol, ethanol, acetaldehyde, acetone, acetic acid, propionic acid, ethylacetate, methane, and ethane. The main reaction products were quantified by GC. No diketones were detected by the reaction with 2,4-dinitrophenylhydrazine. A characteristic absorption spectrum of formaldehyde with chromotropic acid was not obtained (MacFadyen 1945). If formaldehyde is present in the solutions, its concentration must be $\leqslant 1 \times 10^{-7}$ M. Carbon monoxide and hydrogen were not detected by GC.

The more important organic products for the majority of reaction conditions investigated were: propionic acid, methylethylketone, acetic acid, and, in some experiments, acetone and acetaldehyde. Table 3-1 presents the organic product distribution for a series of six experiments using the undoped semiconductor n-TiO$_2$ from Matheson, Coleman and Bell, which was a mixture containing ~70% of the anatase form and ~30% of the rutile (A,R) form as determined by X-ray diffraction. These powders were sieved and the fraction below 50 μ was platinized according to Kraeutler and Bard (1978) using the hydroquinone procedure. The level of platinization was 1%-5%. The experiments were carried out in duplicate to determine the total volume of gas and also what fraction of the gaseous products was carbon dioxide (precipitated as barium carbonate). From the data of Table 3-1, one can observe that without illumination (Expt. A), a minimum amount of thermal decomposition is observed. Platinized anatase:rutile powders gave methylethylketone as the major product according to Eq. 3-1 (Expt. B). The main secondary products were propionic and acetic acids, and acetaldehyde. In the presence of unplatinized anatase rutile powders (Expt. C), the product distribution changes. The amount of carboxylic acids increases by a factor of 2-3. It is interesting to notice that a decrease in the amount of platinized powder added (and therefore total surface area for reaction) also produces a noticeable change in the organic product composition, favoring the formation of propionic and acetic acids (cf. B and D in Table 3-1).

The presence of the carbonyl group in the molecule of levulinic acid leads to additional reactions which seem to involve the C-C bonds adjacent to the carbonyl group. A possible reaction would be the oxidation and cleavage leading to propionic and acetic acids, which can also decarboxylate at the semiconductor/metal interface leading to ethane and methane respectively:

$$H_3C - \underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - COOH \xrightarrow[\text{n-TiO}_2/\text{Pt}]{h\nu} H_3C - COOH + H_3C - CH_2 - COOH$$

$$\downarrow \begin{array}{c} h\nu \\ \text{n-TiO}_2/\text{Pt} \end{array} \qquad \downarrow \begin{array}{c} h\nu \\ \text{n-TiO}_2/\text{Pt} \end{array} \quad (3\text{-}2)$$

$$CH_4 + CO_2 \qquad\qquad C_2H_6 + CO_2$$
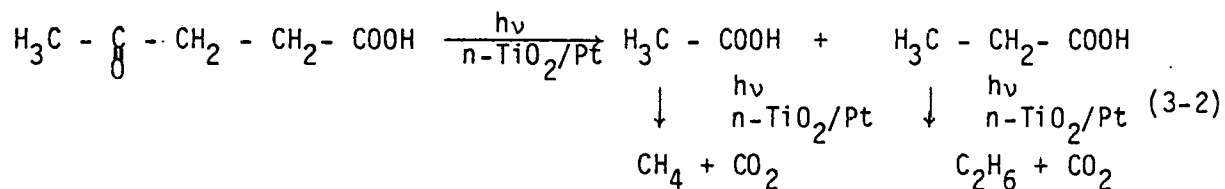
Assuming that CO$_2$ is only produced in the reactions represented by Eqs. 3-1 and 3-2, one can calculate the volume of gas expected for the reactions as a first approximation in Table 3-1, using the mass balance equations:

$$[CO_2] = [CH_3COC_2H_5] + [CH_3COOH]_{dec} + [CH_3CH_2COOH]_{dec} \qquad (3\text{-}3)$$

Table 3-1. Distribution of Products Comparing Experiments in the Dark and upon Illumination of Solutions of Levulinic Acid [2-4 M] in the Presence of Anatase:Rutile [70:30 wt %] (A,R) Powders, at pH = 4.0. Duration of experiments: five hours; at 65°C.

Amount of Products in millimoles	A No Light 6 mg [A,R,Pt][a]/ml	B Light[b] 6 mg [A,R,Pt][a]/ml	C Light[b] 8 mg [A,R]/ml	D Light[b] 1.5 mg [A,R,Pt][a]/ml
CO_2	--	0.69	0.13	~0.3[c]
$CH_3COC_2H_5$	~6 x 10^{-5}	0.66	0.067	0.025
CH_3CH_2COOH	--	0.025	0.056	0.041
CH_3COOH	--	0.011	0.029	0.038
CH_3CHO	--	>0.01	>0.007	>0.02
CH_3COCH_3	~4 x 10^{-5}	0.004	0.002	0.005
V_{gas} collected (ml) 292 K, 620 Torr	0	22	~3	12

[a]A, R, Pt = anatase:rutile (70:30 wt %); platinized with >1 wt % Pt.

[b]In these experiments, 10^{-3} mmoles of methanol and ethanol were also detected. Methane and ethane were also detected among the gaseous products.

[c]Estimated assuming stoichiometric reactions (see text).

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$$[H_3C\text{-}CH_2CO_2H]_T = [H_3C\text{-}CH_2CO_2H]_{soln} + [H_3C\text{-}CH_2CO_2H]_{dec} \qquad (3\text{-}4)$$

$$= [H_3C\text{-}CO_2H]_{dec} + [H_3C\text{-}CO_2H]_{dec}$$

$$\text{mmoles gas} = [CO_2] + [CH_3CO_2H]_{dec} + [CH_3CH_2CO_2H]_{dec} \qquad (3\text{-}5)$$

(soln = in solution; dec = decomposed).

For instance, the total volume for reaction B, Table 3-1 calculated with Eq. 3-5 is 21.6 ml, which compares very well with the experimental volume measured. The ratio of CH_4/C_2H_6 can also be calculated as $[CH_3CO_2H]_{dec}/[CH_3CH_2CO_2H]_{dec}$. For instance, for reaction D this ratio was measured by gas chromatography as 1.4 ± 0.2. The calculated value is 1.0 ± 0.4, in agreement with the observed ratio within the experimental errors.

Acetaldehyde, acetone, methanol, and ethanol could be produced by cleavage and oxidation of the relevant C-C bonds either of levulinic acid or of the decarboxylation product methylethylketone. A few experiments have been carried out by illuminating solutions of methylethylketone containing platinized anatase. The major reaction products detected in these reactions are acetone, acetaldehyde, ethanol, formaldehyde, methanol, and carbon dioxide.

As pointed out by Kraeutler and Bard (1978), adsorption must play a very important role in these reactions. In the case of levulinic acid, there are two sites for adsorption of the molecule to the semiconductor/metal interface. Upon illumination, electron-hole pairs generated can react with the adsorbed material. The reaction products can either be desorbed to solution or react further at the semiconductor/metal interface.

A similar dependence of the nature and ratio of the reaction products on the surface area was also seen in a series of experiments with anatase. Table 3.2 presents data on the distribution of the main organic reaction products obtained when levulinic acid solutions were illuminated in the presence of platinized anatase as a function of pH, surface area, and level of platinization of the powders.

From the data of Table 3-2, it is easily seen that as the level of platinization increases, both the formation of methylethylketone and acetone are favored over the formation of the carboxylic acids (cf. on experiments e and d). A comparison of experiments b and c shows the increase of the amount of carboxylic acids formed as the level of platinization decreases. Similarly, a low surface area powder (Expt. a) produces higher amounts of carboxylic acids.

It is likely that in the experiments with platinized anatase cleavages of the C-C bonds α or β to the carbonyl group are occurring leading, for instance, to acetic acid and, propionic acid or acetone and methanol (or formaldehyde) and carbon dioxide, respectively. Schemes 3.2 and 3.3 summarize the main reaction products.

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Table 3-2. Main Organic Products* Distribution upon Illumination of Levulinic Acid Solutions [2-4 M] Containing 5 mg/ml of Platinized Undoped Anatase as a Function of pH, Surface Area, and Level of Platinization of the Semiconductor. Duration of experiments: 5 hours at 65°C.

	a	b	c	d	e
$[CH_3COCH_2CH_2CO_2H]_{t=0}$, M	4.0	4.0	4.0	2.0	2.0
pH	2.2	3.5	4.0	4.0	4.0

Amount of products in millimoles

	a	b	c	d	e
CO_2	0.27	0.42	0.48	0.42	0.42
$CH_3COC_2H_5$	0.12	0.41	0.11	0.40	~0.03
CH_3CH_2COOH	0.58	0.09	0.65	0.46	0.13
CH_3COOH	0.12	0.01	0.13	0.13	~0.02
CH_3COCH_3	0.12	0.43	0.001	0.10	0.72

a,b,d   low surface area powder, ~1% Pt, prepared according to Kraeutler and Bard (1978).

c   high surface area powder, 0.5% Pt, prepared according to Kraeutler and Bard (1978).

e   high surface area powder, 5% Pt, prepared according to Kraeutler and Bard (1978b).

*Methanol, ethanol, and acetaldehyde were also detected in these experiments in the 10^{-3} mmoles level. Methane and ethane were also detected among the gaseous products.

The participation of free radicals of the type $CH_3COCH_2CH_2\cdot$, $\cdot CH_2CH_2COOH$, $\cdot CH_3$, and $H(C\cdot)O$ has been suggested by Cannistraro et al. (1975) based on electron spin resonance data from irradiated ($\lambda > 220$ nm) frozen levulinic acid solutions (2 M H_2SO_4) in the 77-160 K. It is likely that similar free radicals are intermediates in the photoelectrochemical reactions on n-TiO_2/Pt, though the intensity of the light employed in our experiments is considerably low below 320 nm.

We are presently extending these studies to other semiconductor/metal particulate systems that better match the solar spectrum. We are also extending these investigations to other biomass-derived polyfunctional carboxylic acids.

SCHEME 3.2

$$\left(\overset{O}{\underset{\|}{C}} \cdots \overset{O}{\underset{\|}{C}} OH \right)_{ADS} \;\rightleftharpoons\; \left(\overset{O}{\underset{\|}{C}} \cdots \overset{O}{\underset{\|}{C}}-O^{-} \right)_{ADS}$$

$$\xrightarrow{\text{n-TiO}_2/\text{P}_T,\; h\nu}$$

$$CH_3CH_2\overset{O}{\underset{\|}{C}}OH \xrightarrow[\;h\nu\;]{\text{n-TiO}_2/\text{P}_T} C_2H_6 \;+\; CO_2$$

$$+$$

$$CH_3\overset{O}{\underset{\|}{C}}OH \xrightarrow[\;h\nu\;]{\text{n-TiO}_2/\text{P}_T} CH_4 \;+\; CO_2$$

SCHEME 3.3

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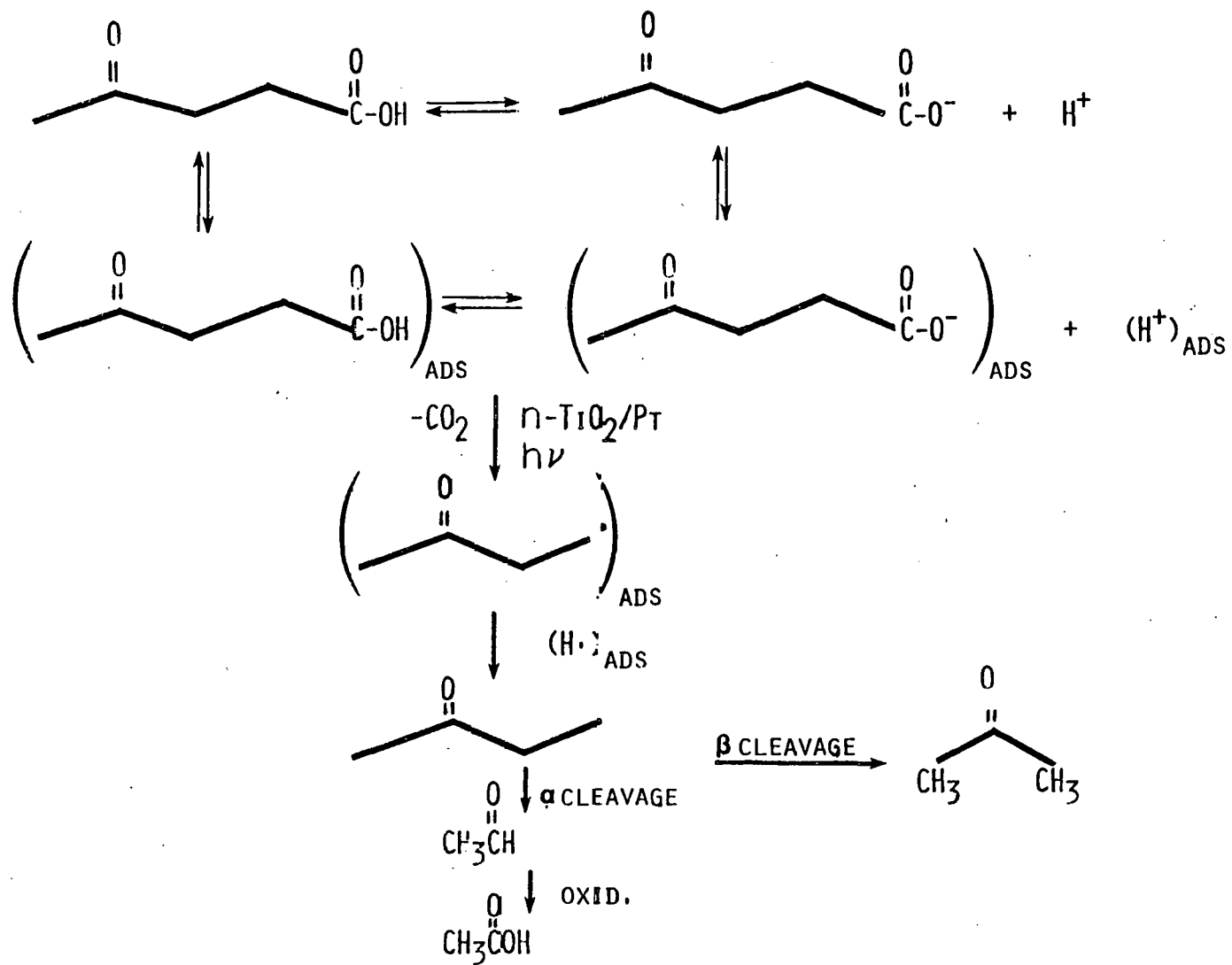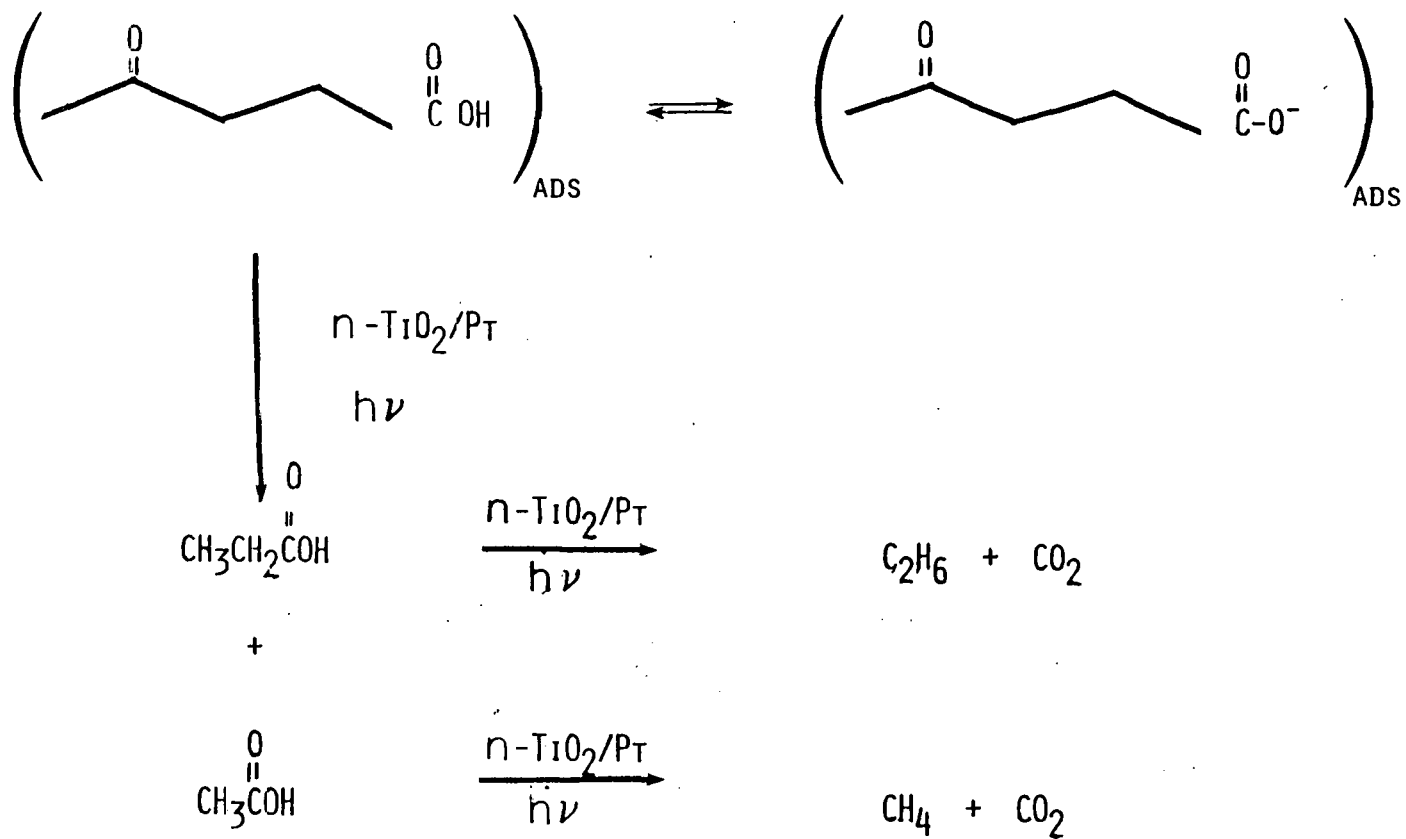
3.3 EXPERIMENTAL SECTION ‡

3.3.1 Materials

Levulinic acid (Aldrich Chemical Co.) was vacuum distilled and recrystallized from 7% $CHCl_3$ in CCl_4. Deuterated water (99.8% Aldrich Chemical Co.) and barium hydroxide (Baker Chemical Co.) were used as received. The TiO_2 powders were anatase (Baker Chemical Co.) confirmed by X-ray diffraction to be >99% anatase, and (Matheson Coleman & Bell) shown to be ~70% anatase and ~30% rutile by X-ray diffraction.* The TiO_2 powders were undoped and platinized by photodecomposition of hexachloroplatinic acid (Baker Chemical Co.) solutions (Kraeutler and Bard 1978 and 1978b).

3.3.2 Apparatus and General Procedure

A 900 W Xe lamp (Model LH 151 N/2 Schoeffel Instrument Corp.) powered by a 1000 W power supply (Model LPS 255 HR Schoeffel Instrument Corp.) operated between 750-850 W was used as the light source. An internal lens was used to focus the light on the reaction cell. The temperature bath and reaction cells were constructed of Pyrex. Several cell designs were tested, the most satisfactory having a test tube end and a flat window (except in those experiments using the <45 μm TiO_2/Pt powders which tended to "plate out" on the window). A typical reaction was performed by illuminating a magnetically stirred slurry of 75-80 mg TiO_2/Pt in 15 ml of 0.5-4 M levulinic acid in D_2O or high purity (organic-compounds-free) H_2O for 5 hours. The slurry and the entire system were purged with argon or nitrogen for a minimum of 20 minutes before illumination and throughout the reaction. The inert gas was admitted via teflon tubing and swept the volatile reaction products out of the cell through a T-bore stopcock fitted to the top of the cell. The gases and volatile products then entered a cold finger condenser immersed in a CO_2/isopropanol filled Dewar and then bubbled through a gas washing bottle filled with 80 ml of saturated $Ba(OH)_2$ solution to precipitate the CO_2 evolved in the reaction as $BaCO_3$ (Kraeutler and Bard 1978a). The $BaCO_3$ was filtered, washed with deionized H_2O, dried at 120°C, and weighed to determine the rate of CO_2 evolution. In some reactions a test tube filled with EtOAc was installed between the cold finger condenser and the gas washing bottle to extract any volatile products not trapped by the cold finger. Several reactions were performed using a volumetric gas collection apparatus, similar to that used by Kraeutler and Bard (1978a) to identify any permanent gases evolved in the reactions. Gas chromatography of the condensed volatile products and of the residual products in the reaction cell was performed on a Porapak Q glass column with a Varian 3700 instrument operated isothermally at 150°C. Permanent gases were analyzed by GC on a carbosieves column. Mass spectral data were obtained using Porapak Q metal columns installed in a Hewlett Packard 5985 GC/MS instrument. NMR spectra were taken on a Jeol FX-90Q instrument.

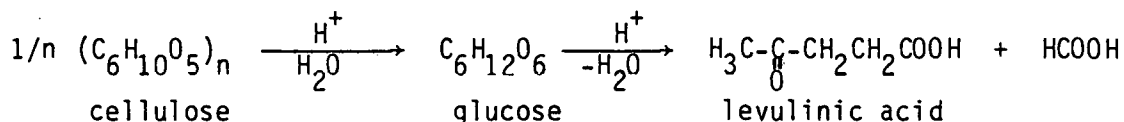
*X-ray diffraction of the powders investigated was performed by Dr. J. Cantrell of the University of Miami (Ohio).

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SECTION 4.0

ELECTROCHEMISTRY OF LEVULINIC ACID AND SELECTED DERIVED COMPOUNDS*

4.1 INTRODUCTION

Levulinic acid is the major product of the controlled degradation of hexose sugars by acids at moderate temperatures (150°C)(McKibbins et al. 1962).

$$1/n \ (C_6H_{10}O_5)_n \ \xrightarrow[H_2O]{H^+} \ C_6H_{12}O_6 \ \xrightarrow[-H_2O]{H^+} \ H_3C-\underset{O}{\overset{}{C}}-CH_2CH_2COOH \ + \ HCOOH$$

$$\text{cellulose} \qquad\qquad \text{glucose} \qquad\qquad \text{levulinic acid}$$

It is produced in high yields, and the recovery of the mineral acid is straightforward (National Research Council Report 1976).

The hexoses, and therefore, levulinic acid, can be obtained from a wide variety of renewable waste products; e.g., wood waste, agricultural waste, waste paper from municipal solid waste, sulfite spent liquor, prehydrolysis liquors from dissolving pulp production, molasses from the sugar industry, etc., or as a by-product of acid hydrolysis of cellulose to fermentable sugars. Since the conversion of these abundantly available raw materials to levulinic acid has been the successfully demonstrated, this compound meets the requirement for a basic raw material. In addition, because of the very reactive nature of the levulinic acid, by virtue of the keto and carboxyl groups, a variety of high value products can be produced. The chemistry of levulinic acid, its pseudo form, and that of the α- and β- angelica lactones, easily formed from levulinic acid, are reviewed by Leonard (1956).

In aqueous acid solutions no polarographic wave is observed for levulinic acid (Nerheim and Estee 1952). Preparative scale constant current electrolyses of the acid have been carried out in several media. In aqueous ethanolic or aqueous sulfuric acid solutions (~25% v/v) on lead or mercury cathodes, levulinic acid is reduced to valeric acid in ~70% yield, with a current efficiency of ~50% (Tafel and Emmert 1911; Motoki and Odaka, 1955). In alkaline solution (~10% w/w NaOH), the reduction on platinum electrodes yields the γ-hydroxyvaleric acid, with 92% current efficiency. This acid cyclizes during isolation to give γ-valerolactone in 60% yield (Tafel and Emmert 1911). The reduction of nitrobenzene in the presence of levulinic acid leads to the synthesis of 5-methyl-1-phenyl-2-pyrrolidone (Emmert 1907).

The Kolbe electrolyses of levulinic acid have been utilized to synthesize diketones; e.g., 2,7-octanedione in 50-60% yield (Hofer 1900; Shimizu 1950). A number of other aliphatic diketones were synthesized in 20%-30% yields from

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*D.W. Sopher, M. Ratcliff, A. Hauser (Summer Intern), and H.L. Chum.

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the electrolyses of mixtures of carboxylic and levulinic acids (Motoki and Odaka 1945; Tsusuki and Motoki 1956). Many higher oxoacids have also been synthesized by Kolbe electrolyses of monomethyl esters of dicarboxylic acids and levulinic acid (Motoki and Odaka 1956 and 1960; Tsusuki et al. 1957). The by-product of all these reactions is the 2,7-octanedione.

During the past year we have addressed the dark electrochemistry of levulinic acid and ethyl levulinate. The aim of these studies is to attempt to realize a novel electrochemical synthetic dimerization of the carbonyl compound leading to a pinacol. By hydrogenation of this pinacol derivative, one could obtain 4,5-dimethyloctan-1,8-diol. Such a compound could be used to promote the solubility of lower alcohols in diesel fuel or could be dehydrated to give an α, ω olefin for use as a crosslinking agent in polymers (Scheme 4.1). In addition, we have examined briefly the electrochemical reduction of levulinic acid to valeric acid, since it is known that the Kolbe electrolyses of valeric acid on carbon electrodes leads to mainly butene-1, butylpentanoate, butanol, and octane (e.g., Koehl 1964). All of these compounds can be separated from the solution easily due to their physical properties. Butene-1 is an important petrochemical feedstock. The other compounds can be fuel additives. An economic assessment of such syntheses has not been carried out. It is to be expected that the pinacolization process proposed would be very favorable from an electric energy consumption standpoint (one Faraday per mole process and no mass loss during the process). A relatively low-volume, high-value product would result from renewable resources. The synthesis of levulinic acid from valeric acid, followed by anodic oxidation of valeric acid to the products mentioned above would consume more electric energy than the previous process and also have a built-in mass loss in the process (e.g., CO_2 in the anode compartment).

4.2 REDUCTIVE COUPLING OF CELLULOSE-DERIVED ALKYL LEVULINATES

The electrochemical reductive dimerization of aldehydes and ketones is well known (Baizer 1973) and has been used to prepare vicinal diols on an industrial scale (Beck 1974).

In the cyclic voltammetry (EtOH/TBAP; Hg drop) of levulinic acid only hydrogen evolution is observed at potentials below that of solvent reduction. Similarly, lithium levulinate shows no peaks in voltammetry due to carbonyl group reduction. Conversion of levulinic acid to the ethyl ester, however, lowers the reduction potential of the 4-keto group to below that of the solvent cut-off (EtOH/TBAP and DMF/TBAP; Hg drop; Fig. 4-1). Reductive coupling of ethyl levulinate would lead to a dimeric compound which upon catalytic hydrogenation would be converted into 4,5-dimethyloctan-1,8-diol (Scheme 4.1).

Strong alkaline or acid conditions in nonaqueous solvents have been often used in the literature to promote the reductive coupling of carbonyl compounds (Baizer 1973). Preparative scale controlled potential electrolyses have been carried out in ethanol/tetrabutyl ammonium perchlorate (TBAP), ethanol/10% H_2SO_4, and DMF/TBAP at a mercury pool cathode. A 2 Fmol^{-1} process took place in ethanol/TBAP to give γ-valerolactone as the only reduction product (Scheme
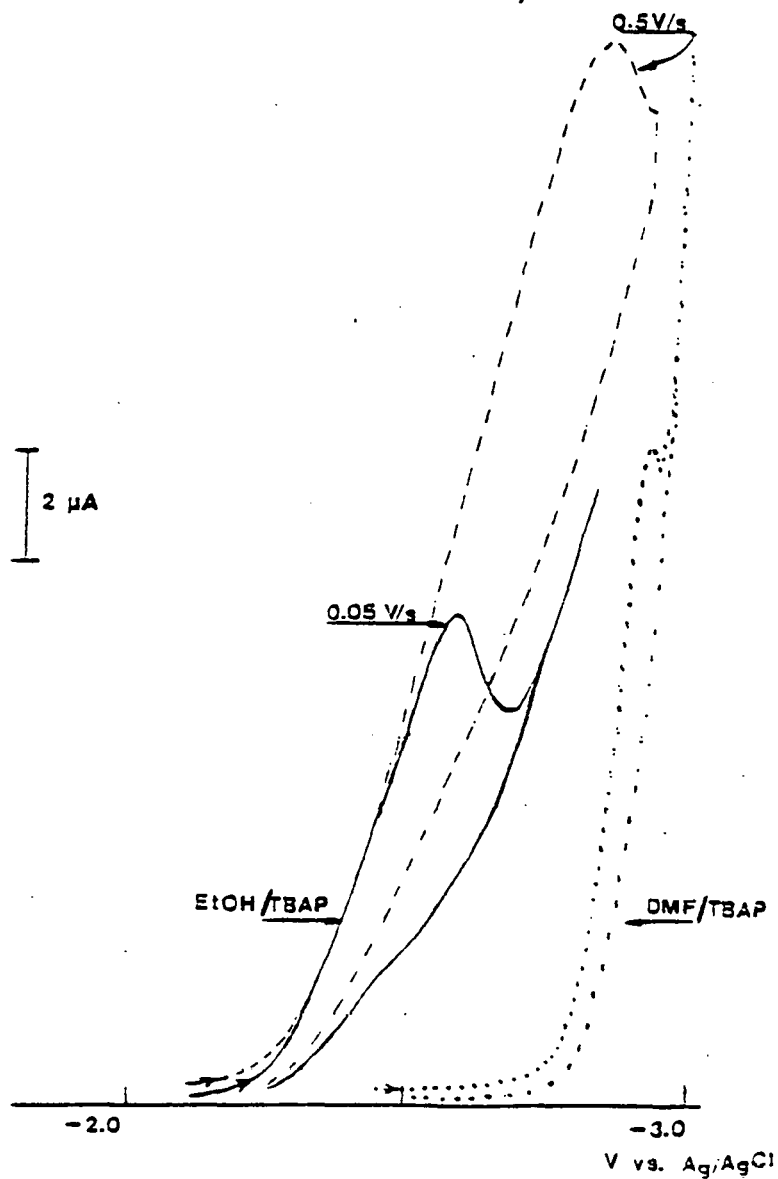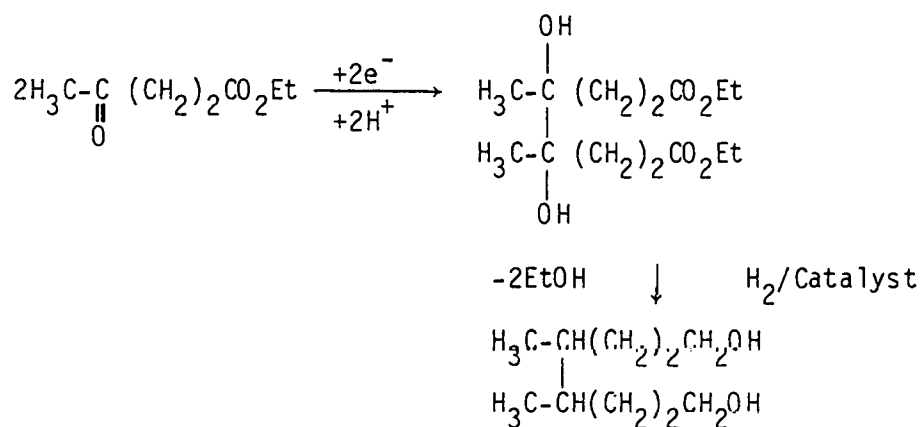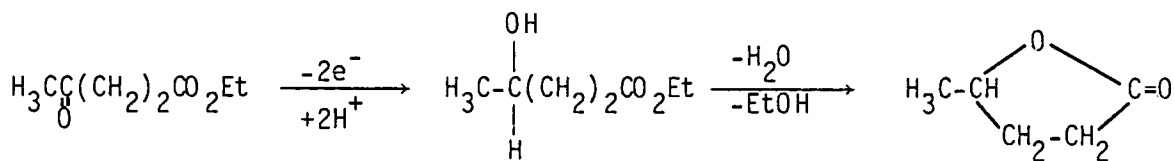
Figure 4-1. Cyclic Voltammograms of 1.5 x 10^{-3} Solutions of Ethyl Levulinate in Ethanol (EtOH) or Dimethylformamide (DMF) Containing Tetrabutylammonium Perchlorate on a Hanging Mercury Drop Electrode. Voltammograms are not corrected for ohmic drop.

4.2). In DMF/TBAP, however, a 1 $Fmol^{-1}$ process occurred and two reduction products were isolated: γ-valerolactone and an as yet not fully identified carboxylic acid which appears from mass spectral results to be dimeric. In ethanol/10% H_2SO_4, the reduction reaction of the keto compound to a dimeric compound appears to have occurred also. Other products detected included γ-valerolactone and levulinic acid, indicating that chemical hydrolysis of the ester was also taking place. It is important to point out that all the reaction conditions tested (strong alkaline and strong acid) lead to several possible side reactions, both chemical and electrochemical. Since the hydrogen atoms on the methylene groups between the carbonyl and the carboxyethyl groups are acidic, there is a possibility of generation of bases in nonaqueous solvents, probably at the electrode surface. Condensation reaction involving such bases and the carbonyl compounds are possible reactions. In strong acid, a competition between the desired organic electrochemical reaction and hydrogen evolution takes place. Due to the high reactivity of the ethyl levulinate molecule, we are carrying out electrolyses of this keto ester in more mild conditions in nonaqueous solvents to attempt to maximize the desired dimerization reaction and to minimize side reactions, both chemical and electrochemical.

$$2H_3C-\underset{O}{\overset{\parallel}{C}}(CH_2)_2CO_2Et \xrightarrow[+2H^+]{+2e^-} \begin{array}{c} OH \\ | \\ H_3C-\underset{|}{\overset{}{C}}(CH_2)_2CO_2Et \\ H_3C-\underset{|}{\overset{}{C}}(CH_2)_2CO_2Et \\ OH \end{array}$$

$$-2EtOH \quad \downarrow \quad H_2/Catalyst$$

$$\begin{array}{c} H_3C-\underset{|}{\overset{}{CH}}(CH_2)_2CH_2OH \\ H_3C-\underset{}{\overset{}{CH}}(CH_2)_2CH_2OH \end{array}$$

Scheme 4.1 Proposed Reductive Coupling of Ethyl Levulinate

$$H_3C\underset{O}{\overset{}{C}}(CH_2)_2CO_2Et \xrightarrow[+2H^+]{-2e^-} \begin{array}{c} OH \\ | \\ H_3C-\underset{|}{\overset{}{C}}(CH_2)_2CO_2Et \\ H \end{array} \xrightarrow[-EtOH]{-H_2O} H_3C-CH\overset{O}{\underset{CH_2-CH_2}{\diagup\diagdown}}C=O$$

Scheme 4.2 Reduction of Ethyl Levulinate

4.3 REDUCTION OF LEVULINIC ACID

Preparative scale constant potential and constant current electrolyses of levulinic acid (1-3 M) in sulfuric acid (0.1-1 M) have been carried out on

lead cathodes. The constant potential electrolyses were performed in a static cell whereas the constant current electrolyses were carried out in a modified parallel plate flow cell (Electroprep cell). The overall electrochemical reduction reaction observed was:

$$H_3C\text{-}\underset{\underset{O}{\|}}{C}(CH_2)_2COOH \xrightarrow[+4H^+]{+4e^-} H_3C\text{-}(CH_2)_3COOH + H_2O$$
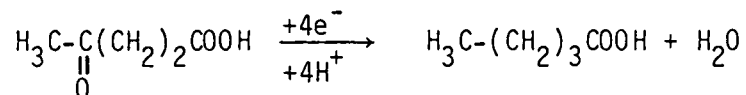
with hydrogen evolution as the side reaction. Current efficiency measurements have been performed under a variety of conditions which are listed in Table 4-1. From these data the reduction process is very efficient at conversions of levulinic to valeric acid up to 30%. As expected, the efficiencies are higher at lower conversions. These results are higher than the 50% current efficiency and 70% yield of valeric acid previously reported in the literature (Tafel and Emmert 1911). From our data, an electrochemical process based on this reduction reaction appears highly feasible.

We are addressing the separation of levulinic and valeric acids, hoping to achieve a built-in separation in the electrochemical process.

Table 4-1. Current Efficiency for the Electrochemical Reduction of Levulinic Acid to Valeric Acid on Lead Cathodes at 30% Conversion.

Static Cell
Constant—Potential -1.8 V vs. Ag/AgCl, 50°C

$[H_2SO_4]$, M	$[H_3CCO(CH_2)_2COOH]$, M	Current Efficiency, %
1.0	1.0	98
0.1	1.0	82

Parallel Plate Flow Cell
$[H_2SO_4]$ = 1.0 M; Flow Rate = 40-60 ml/min; 30°C

Current Density mA/cm^2	$[H_3CCO(CH_2)_2COOH]$ M	Current Efficiency, %
55	1.0	>90
110	1.0	80
200	3.0	90

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4.4 EXPERIMENTAL SECTION

All constant potential electrolyses of ethyl levulinate have been carried out with the cell described in Sec. 2.3. The separation of electrolyses products in the pinacolization reaction has been carried out by solvent extraction or by medium pressure liquid chromatography using silica gel columns. The potentiostats employed are also described in Sec. 2.3. Mass spectra of the reaction products were obtained using the GC/MS spectrometer Hewlett Packard 5985.

The parallel plate flow cell employed in the reduction of levulinic acid was the Electroprep cell, obtained from ECO Inc., and modified to operate with lead cathodes and lead dioxide anodes. The lead cathode was pretreated by preelectrolysis in 1 M H_2SO_4 alternating the electrode polarity. The static cell employed in the reduction of levulinic acid consisted of parallel disc electrodes [lead (Alfa) and graphite (Alfa)] separated by a sintered glass frit, similar to the cell described by Dubois et al. (1970).

The concentrations of valeric and levulinic acids were determined as a function of the extent of the reaction by UV-visible absorption spectroscopy using a Hewlett-Packard 8450A spectrophotometer.

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SECTION 5.0

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