Photoelectrochemistry of Levulinic Acid on Undoped Platinized n-TiO₂ Powders

H. L. Chum.*[†] M. Ratcliff.[†] F. L. Posev.[†] J. A. Turner.[‡] and A. J. Nozik[‡]

Thermochemical and Electrochemical Research Branch and Photoconversion Research Branch, Solar Energy Research Institute, Golden, Colorado 80401 (Received: November 15, 1982)

The photoelectrochemistry of levulinic (4-oxopentanoic) acid, the major product of controlled degradation of cellulose by acids, has been investigated. 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 platinized undoped n-TiO₂, as anatase, anatase-rutile mixture, or rutile. The effects of the level of platinization, pH, acid concentration, and the semiconductor surface area were investigated. In addition to the decarboxylation reaction leading to methyl ethyl ketone, we have also observed novel cleavages of the C-C backbone leading to propionic acid, acetic acid, acetone, and acetaldehyde as major products. These lower molecular weight carboxylic acids undergo decarboxylation at the slurry diodes to ethane and methane. The organic product distribution is a complex function of the crystallographic phase of $n-TiO_2$ and of the level of metallization of the semiconductor powder.

Introduction

Photoelectrochemical systems utilizing various semiconducting materials are currently of interest principally when they can utilize sunlight (0.9-3.2 eV per photon) for the production of electrical energy or to produce useful chemicals.¹⁻⁵ Photoelectrosynthetic systems that consist of microscopic semiconductor particles suspended in the solution of the reactive substrate are potentially a very simple approach to carry out photoelectrocatalytic or synthetic reactions. The most effective particulate systems to date 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.³ The first type of heterogeneous systems, in the form of 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) powders.⁶ 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.³

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.⁷ 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 Fe₂O₃.⁸ 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.⁹ Strontium titanate powders were shown to photoreduce carbon dioxide to methanol and traces of formaldehyde.¹⁰

Examples of reactions driven by heterogeneous semiconductor/metal photochemical diodes include nitrogen reduction to ammonia by using a single-crystal p-GaP/Al system,¹¹ decarboxylation of carboxylic acids¹²⁻¹⁴ on platinized doped and undoped n-TiO₂ (anatase and rutile), and water splitting (extensively reviewed in ref 1-5). Methane was observed as the reduction product of carbon

dioxide on Pt/SrTiO₃(III).¹⁵ The heterogeneous photosynthetic production of amino acids at platinized TiO₂ suspensions by near-UV light from CH₄-NH₃-H₂O mixtures was also investigated.¹⁶ It is interesting that the reverse reaction, the photocatalyzed decomposition of amino acids on metal oxides (some of which are semiconducting),¹⁷ yields NH₃, glyoxylic acid, acetaldehyde, and formaldehyde.

Some heterogeneous photocatalytic reactions on semiconductor particulate systems involving more complex organic substrates have also been investigated. Upon irradiation, oxygenated suspensions of TiO2 and toluene yielded benzaldehyde, cresols, and bibenzyl, which are also the products found in the reaction of toluene with the Fenton reagent;¹⁸ hydrocarbons are oxidized to CO₂ with intermediate production of hydroxylated compounds.¹⁹ Upon irradiation of glucose solutions containing platinized doped anatase powders, hydrogen and carbon dioxide are formed.²⁰ These results are similar to those obtained by Kawai and Sakata²¹ with ternary powder systems

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[‡]Photoconversion Research Branch.

 $RuO_2/TiO_2/Pt$ on starch, cellulose, and sucrose. Fox and Chen²² investigated photocatalyzed α -pinene (olefin-tocarbonyl) oxidative cleavage on TiO₂ and CdS semiconductor electrodes. Photocatalytic oxidations of lactams and N-acyl amines have been reported.²³

In 1978, Kraeutler and Bard¹² described a new Kolbe reaction pathway, obtained when acetate solutions are irradiated in the presence of particulate photochemical diodes of $n-TiO_2/Pt$. The major product of the reaction was methane; ca. 10% of ethane, the Kolbe product, along with some hydrogen were also detected. The platinized semiconductor particles act as short-circuited electrodes. Illumination with light of energy greater than the band gap (>3-3.2 eV) of the semiconductor causes the formation of electron-hole pairs. The recombination of the electronhole pairs is partially prevented by the following fast (irreversible) chemical reactions. The holes oxidize acetate ions to CH_3CO_2 radicals, which rapidly decompose to methyl radicals and carbon dioxide, while the electrons reduce protons of the solvent to hydrogen. The byproduct hydrogen and isotopic substitution pattern indicate that the methane formed is a result of the reaction between methyl radicals and hydrogen (from the solvent). This investigation was extended¹³ to other saturated carboxylic acids, namely, propionic, butyric, valeric, pivalic, and adamantane-1-carboxylic. All of these acids were photoelectrochemically decarboxylated to the corresponding hydrocarbons. The participation of free-radical intermediates was observed through electron spin resonance.²⁴ Kraeutler and Bard¹³ 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.

This paper describes the photoelectrochemical reactions involving a simple polyfunctional carboxylic acid, namely, 4-oxopentanoic (levulinic) acid on platinized, undoped, n-TiO₂ particulate systems. Such acid is present in waste streams of cellulose acid hydrolysis plants.²⁵

Experimental Section

Materials. Levulinic acid (Aldrich Chemical Co.) was vacuum distilled and recrystallized from 7% CHCl₃ in CCl₄. 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 rutile-anatase mixtures (Matheson Coleman and Bell) shown to be $\sim 70\%$ anatase and $\sim 30\%$ rutile by X-ray diffraction (X-ray diffraction of the powders was performed by Dr. J. Cantrell of Miami University (Ohio)). The TiO_2 powders were undoped and platinized by photodecomposition of hexachloroplatinic acid (Baker Chemical Co.) solutions.^{12,23} The platinum and titanium contents of the powders were determined by the Colorado School of Mines Research Institute by atomic absorption after dissolution in fuming sulfuric acid.

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 and 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, and most satisfactory having a test tube end and a flat window (except in those experiments using the $<45-\mu m \operatorname{TiO}_2/\operatorname{Pt}$ powders which tended to "plate out" on the window). A typical reaction was performed by illuminating a magnetically stirred slurry of 75-80 mg of 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 h. The slurry and the entire system were purged with argon or nitrogen for a minimum of 20 min 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 $CO_2/2$ -propanol-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 $BaCO_3$. The $BaCO_3$ was filtered, washed with deionized H_2O , dried at 120 °C, and weighed to determine the total 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 by using a volumetric gas collection apparatus, similar to that used by Kraeutler and Bard¹³ to identify any permanent gases evolved in the reactions.

After the photoelectrochemical experiments, the contents of the suspensions were cooled to ~ 5 °C and transferred to a centrifuge tube. The supernatant was analyzed and the powders were washed 2-3 times in water (and finally in acetone) by ultrasonic resuspension followed by centrifugation (15000 rpm, 10 min). Powders that had been reused 4-5 times appeared to have lost some of the platinum catalyst. All of the quantitative analytical data reported here on duplicate experiments used the same batch of previously unused platinized powder. The platinum content within the same batch of powder may vary within 20% (the analytical error for $\sim 5\%$ content of Pt is 5%) prepared according to ref 23. Powders prepared according to ref 12 had, in general, lower platinum content (0.2-1.5%) and seemed to be more stable toward mechanical degradation.

Gas chromatography of the condensed volatile products of the residual products in the reaction cell was performed on an 80/100 mesh Porapak Q glass column (6 ft \times 4 mm i.d.). The analysis was performed with a Varian 3700 gas chromatograph operated at a column temperature of 140 °C, a flow rate of 30 mL/min, and with a flame ionization detector. The permanent gases were determined by gas chromatography using a 6 ft \times 2 mm i.d. stainless-steel column packed with Carbosieve S. The analysis was temperature programmed under the following conditions: 35 °C, 4-min hold; increased temperature to 150 °C at a rate of 10 °C/min; flow rate, 20 mL/min, helium; detector, thermal conductivity 205 MA; range, 0.05 mV. The component concentrations were calculated by the external standard method.

Mass spectral data were obtained on the Hewlett-Packard 5985 GC/MS, using either the Porapak Q or the Carbosieve S column coupled to the mass spectrometer (electron impact mode). GC and mass spectral assignments were verified by injecting the authentic pure compounds and comparing their retention times and fragmentation patterns with those of the reaction products. The library editor program for probability based search of the HP5985 GC/MS system was also used in the identification of the reaction products.

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Figure 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 ($A \ge 1\%$ Pt, (5 mg of Pt/TiO₂)/(mL of solution), experiments 15, 18, 19, 35, and 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.

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 has been investigated.

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-TiO₂ powders, but in the absence of illumination, is 0–0.5 μ mol/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-TiO₂ (as anatase, or a mixture of anatase and rutile, or rutile) appreciable evolution of carbon dioxide occurs, 10–150 times faster than in the thermal or photoblank experiments. The rates depend on the crystallographic phase of n-TiO₂, the level of platinization of the semiconductor, pH, and the levulinic acid concentration (see Figures 1 and 2).

The rate of carbon dioxide evolution decreased slightly as the concentration of acid decreased from 4 to 2 M (see Figure 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 and 37) in 2 M levulinic acid. For the platinized powders, the rate of CO₂ evolution of the anatase-rutile mixture is somewhat larger than that of anatase (cf. experiments 15, 28, and 36). Both anatase and anatase-rutile mixtures have 5-8 times larger decarboxylation rates than the pure rutile phase of n-TiO₂. This is likely due to the slightly larger band gap of anatase (3.2 eV) which gives it a slightly more negative conduction band, thereby enhancing the water reduction reaction.

The effect of pH on the rate of decarboxylation is shown in Figure 2. The data were obtained at 2 or 4 M levulinic acid. The Pt loading of the semiconductor powders used



Figure 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 of Pt/TiO₂)/(mL of solution)) at 65 °C.

in these experiments ranged from 1% to 5%. A pH dependence similar to that obtained by Kraeutler and Bard¹³ for acetic acid is observed for levulinic acid. Whereas for acetic acid the optimum pH for decarboxylation was 3.5,¹³ in our experiments the optimum pH is 4.0, consistent with the fact that levulinic acid is about a 2.3 times stronger acid than acetic acid.

At pH 3.5 experiments were performed with slurries containing less than 1% platinum loading. At 1% the rate of decarboxylaaion is ~80 μ mol/h. At 0.2%, the rate of decarboxylaion decreases to 55 μ mol/h; with a loading of 0.04%, the rate decreased to 45 μ mol/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.

Organic Product Distribution. The expected product of the photoelectrochemical decarboxylation of levulinic acid on n-TiO₂ powders is methyl ethyl ketone if a decarboxylation reaction similar to that observed by Kraeutler and Bard^{12,13} for aliphatic carboxylic acids occurs:

$$\begin{array}{c} H_{3}CCC_{2}H_{4}CO_{2}H \xrightarrow{\hbar\nu} H_{3}CCC_{2}H_{5} + CO_{2} \\ \parallel \\ 0 \\ \end{array}$$

Indeed, this ketone was identified as one of the organic reaction products in all experiments performed with levulinic acid and n-TiO₂. However, in addition to this expected product, several volatile organic compounds were identified by GC/MS: methanol, ethanol, acetaldehyde, acetone, acetic acid, propionic acid, ethyl acetate, 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.²⁷ If formaldehyde is present in the solutions, its concentration must be $\leq 1 \times 10^{-7}$ 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, methyl ethyl ketone, acetic acid, and, in some experiments, acetone and acetaldehyde. Table I presents the organic product distribution for a series of six experiments using the undoped semiconductor n-TiO₂ from Matheson Coleman and Bell, which was a mixture containing $\sim 70\%$ of the anatase form and $\sim 30\%$ of the rutile (A,R) form. These powders were sieved and the fraction below 50 μ m was platinized according to Kraeutler and Bard¹² using the hydroquinone procedure. The level of platinization was

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TABLE I: Distribution of Products ComparingExperiments in the Dark and upon Illumination ofSolutions of 2-4 M Levulinic Acid in the Presence of70/30 wt % Anatase-Rutile (A,R) Powders at pH 4.0^a

	A ^b	$\mathbf{B}^{c,f}$	$C^{d,f}$	$\mathbb{D}^{e,f}$	
CO ₂ , mmol	ND^h	0.69	0.13	~0.3g	
CH ₃ COC,H ₃ , mmol	$\sim 6 \times 10^{-5}$	0.66	0.067	0.025	
CH ₃ CH ₂ COOH, mmol	ND	0.025	0.056	0.041	
CH ₃ COOH, mmol	ND	0.011	0.029	0.038	
CH ₃ CHO, mmol	ND	>0.01	>0.007	>0.02	
CH ₃ COCH ₃ , mmol	$\sim 4 \times 10^{-5}$	0.004	0.002	0.005	
$V_{\rm gas}$ collected (292 K,	0	22	~3	12	
620 torr), mL					

^a Duration of experiments: 5 h at 65 °C. (A,R,Pt) = anatase-rutile (70/30 wt %), platinized with >1 wt % Pt. ^b No light, 6 mg of (A,R,Pt)/mL. ^c Light, 6 mg of (A,R,Pt)/mL. ^d Light, 8 mg of (A,R)/mL. ^e Light, 1.5 mg of (A,R,Pt)/mL. ^f In these experiments, 10^{-3} mmol of methanol and ethanol was also detected. Methane and ethane were also detected among the gaseous products. ^g Estimated by assuming stoichiometric reactions (see text). ^h ND = not detected within experimental error.

 $\sim 1\%$. 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 I, one can observe that without illumination (experiment A), a minimum amount of thermal decomposition is observed. Platinized anatase-rutile powders gave methyl ethyl ketone as the major product according to eq 1 (experiment B). The main secondary products were propionic and acetic acids, and acetaldehyde. In the presence of unplatinized anatase-rutile powders (experiment 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 I).

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

 $H_{3}CCCH_{2}CH_{2}COOH \xrightarrow{h\nu} H_{3}CCOOH + H_{3}CCH_{2}COOH + H_{3}CCH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH$

Assuming that CO_2 is produced only in the reactions represented by eq 1 and 2, one can calculate the volume of gas expected for the reactions as a first approximation in Table I, using the mass balance equations: [CO₂] =

$$[C\dot{H}_{3}COC_{2}H_{5}] + [CH_{3}COOH]_{dec} + [CH_{3}CH_{2}COOH]_{dec}$$
(3)

$$[H_3CCH_2CO_2H]_T = [H_3CCH_2CO_2H]_{soln} + [H_3CCH_2CO_2H]_{dec} = [CH_3CO_2H]_T = [H_3CCO_2H]_{soln} + [H_3CCO_2H]_{dec}$$
(4)

mmol of gas =

$$[\tilde{CO}_2] + [CH_3CO_2H]_{dec} + [CH_3CH_2CO_2H]_{dec}$$
(5)

(soln = in solution: dec = decomposed). For instance, the total CO₂ volume for reaction B, Table I, calculated with eq 5 is 21.6 mL, which compares very well with the experimental volume of 22.0 mL 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 methyl ethyl ketone. A few experiments have been carried out by illuminating solutions of methyl ethyl ketone containing platinized anatase. The major reaction products detected in these reactions are acetone, acetaldehyde, ethanol, formaldehyde, methanol, and carbon dioxide. None of the expected dimerization products of photochemical reactions of methyl ethyl ketone have been found. The photoelectrochemical reaction promotes the novel β -cleavage leading to acetone as a major product.

A dependence of the nature and ratio of the reaction products on the surface area was also seen in a series of experiments with anatase (cf. Table I). Table II 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 II, it is easily seen that, as the level of platinization increases, the formation of both methyl ethyl ketone and acetone is favored over the formation of the carboxylic acids (cf. 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 (experiment a) produces higher amounts of carboxylic acids.

Inspection of Tables I and II reveals that the distribution of organic products in the photoelectrochemical reactions of levulinic acid on platinized n-TiO₂ semiconductor is a quite complex function of the crystallographic phase of the semiconductor, level of platinization, surface area, concentration of levulinic acid, and pH. At the optimum pH for decarboxylation, methyl ethyl ketone is the major

TABLE II:Main Organic Products Distribution upon Illumination of 2-4 M Levulinic Acid Solutions Containing 5 mg/mLof Platinized Undoped Anatase as a Function of pH, Surface Area, and Level of Platinization of the Semiconductor^a

	а	р	с	d	е	
$[CH_{3}COCH_{2}CH_{2}CO_{2}H]_{t=0}, M$	4.0	4.0	4.0	2.0	2.0	
pH	2.2	3.5	4.0	4.0	4.0	
CO ₂ , mmol	0.27	0.42	0.48	0.42	0.42	
CH ₃ COC, H ₅ , mmol	0.12	0.41	0.11	0.40	~0.03	
CH ₃ CH ₂ COOH, mmol	0.58	0.09	0.65	0.46	0.13	
CH,COOH, mmol	0.12	0.01	0.13	0.13	~0.02	
$CH_{3}COCH_{3}$, mmol	0.12	0.43	0.001	0.10	0.72	

^a Duration of experiments: 5 h at 65 °C. a, b, d: low surface area powder, $\sim 1\%$ Pt.¹² c: high surface area powder, 0.5% Pt.¹² e: high surface area powder, 5% Pt, different preparation.²⁵ Methanol, ethanol, and acetaldehyde were also detected in these experiments in the 10⁻³ mmol level. Methane and ethane were also detected among the gaseous products.

product on platinized anatase_rutile (see Table I, B) but cleavage of the C-C bond β to the carbonyl group is more important on platinized undoped anatase powders, leading to acetone as the major organic product (Table II, b and e). Lower levels of platinization tend to favor the cleavage α to the carbonyl leading to the mixture of acetic and propionic acids, which can also undergo further decarboxylation.

The change in product distribution and total product formation with decreasing amounts of semiconductor/ metal particles suggests that adsorption must play an important role in these reactions. The bifunctional molecule of levulinic acid has two sites for adsorption. It is also possible that, at the level of the electrode, the enol form might be present and adsorbed on the semiconductor. Large changes in product distribution are also observed as the level of platinization decreases, leading to a larger extent of the cleavage of the C-C backbone in a position α to the carbonyl (of Table I, B and C, and Table II, b and c). This same cleavage is favored as the pH decreases (Table II, a and b). It appears that under these circumstances the carbonyl adsorption may prevail and lead to preferential backbone cleavage.

The mechanism of the photoelectrochemical reactions of levulinic acid on undoped platinized n-TiO₂ powders may involve direct reaction of the photogenerated holes (and electrons) with the adsorbed acid leading to the fomation of free radicals (e.g., $H_3CCO(CH_2)_2COO$) observed in the irradiation of frozen H_2SO_4 glasses of levulinic acid with UV light²⁸ or, more likely, the reaction can be indirect through the reaction of water with the photogenerated holes and electrons:

$$(\text{TiO}_2) + h\nu \rightarrow e^- + h^+$$
$$\text{H}_2\text{O} + h^+ \rightarrow \text{HO} + \text{H}^+$$
$$\text{H}^+ + e^- \rightarrow \text{H} \cdot$$

The very powerful oxidizing agent, HO· radicals,²⁹ possibly adsorbed at the semiconductor surface, could then react with adsorbed molecules of the organic acid. Since this acid can be adsorbed at either of two sites (COO⁻ or C—O), the radical attack on either the carboxyl or the C—C bond adjacent to the carbonyl group would lead to the observed reaction products. The participation of the less powerful oxidizing agent, HO_2 radicals, may also be involved in this reaction. It is likely that a stronger adsorption of levulinic acid on the mixture of anatase and rutile than on anatase alone could explain higher yields of products in the former mixture compared to the anatase reactions.

It is interesting to report that, when the photoelectrochemical reactions of levulinic acid were carried out on α -ferric oxide, a product distribution similar to that found on unplatinized anatase-rutile mixture was found, i.e., large amounts of propionic and acetic acids, as well as methyl ethyl ketone. We are continuing the investigation of organic acid substrates on ferric oxide and other semiconducting powders.

Conclusion

The photoelectrochemical reactions of the bifunctional carboxylic acid on platinized undoped n-TiO₂ is very complex both in product distribution and in the interrelationship of reaction parameters. The crystallographic phase of n-TiO₂ plays an important role, and the mixture of platinized undoped anatase and rutile was shown to give higher yields of products than anatase alone. The method of platinization and the level of platinization have also been shown to be important in determining product distribution. Surface area also plays an important role in these reactions. By changing the ratio of crystallographic phases it was possible to drive the reaction to mainly methyl ethyl ketone or to acetone, methane, and ethane. Further investigation in this area should employ powders with better surface characterization and with homogeneous metallization. This paper shows that interesting new reactions can be driven by particulate photochemical diodes. Deeper understanding of the relationship between the various parameters and the reaction products is necessary, in order to make these reactions occur at much higher rates and yields.

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Registry No. Levulinic acid, 123-76-2; anatase, 1317-70-0; rutile, 1317-80-2; titanium dioxide, 13463-67-7; platinum, 7440-06-4.

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