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Potentiostatic Anodic Acetoxylation Reaction of Phenylacetic Acid

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Electrooxidation of phenylacetic acid in CH_3COOH/CH_3COOK at pH 5.2 under potentiostatic condition was investigated at Pt gauze, amorphous carbon and chemically modified (Ti/TiO_2 silanized) electrodes. Products obtained during the study have been explained in the light of electrocatalysis.

INTRODUCTION

Electrochemical oxidation of phenylacetic acid in methanol-pyridine mixture[1] and pure methanol[2] has been reported at platinum electrode to result in dibenzyl. Ross and Finkelstein[3] extended this work by differentiating reaction path at various electrodes viz., platinum and carbon anodes by using different media, for instance 67% methanol-33% pyridine and 67% water-33% pyridine to a variety of products. Anodic acetoxylation reaction has been investigated by Eberson and Nyberg[4] for a number of aromatic compounds. This communication presents oxidation of phenylacetic acid in acetic acid-potassium acetate at chemically modified Ti/TiO_2, platinum gauze and amorphous graphite anodes.

EXPERIMENTAL

Phenylacetic acid (Aldrich) was further recrystallized from 50% ethanol (m.pt. 77°). Acetic acid, potassium acetate BDH(AR) and trimethoxyvinylsilane (98% Aldrich) were used without further purification.

Laboratory scale electrolysis was carried out in a divided glass cell at a potential controlled by Wenking Potentiostat Model LB 81 M. Graphite rod having surface area $\simeq 4.1\ cm^2$, platinum gauze ($A = 3.8\ cm^2$) and chemically modified (Ti/TiO_2 silanized, $A = 2 \times 2\ cm^2$) electrode served as anodes while Cu plate $2 \times 2\ cm^2$ was used as cathode. Reference electrode $Ag/AgCl/Cl^-$ was connected to the anode compartment with a Luggin capillary in order to measure potential of working electrode accurately. Agitation of electrolytic mixture was performed with a magnetic stirrer at 1000 rpm. Electrolytic solution was adjusted at pH 5.2 (unless specified otherwise). Ultrathermostat NBE (Germany) was employed to maintain a temperature of $22 \pm 1°$. Four parts of solution of acetic acid containing 0.2 M potassium acetate was placed in anode compartment and one part in cathode compartment. Phenylacetic acid (0.1 M) was added only to anode compartment and electrolysis was conducted at +1.85 V having initial current 200 mA. Electrolysis was continued till cell current decayed to 10 mA which generally took on an average 25 hrs. Cyclic voltammetric measurements were made at 0.4 cm^2 graphite working electrode, using Tektronix Cathode Ray Oscilloscope, Type 541, Oregon, U.S.A. During the investigation pH of solution was recorded by Trombay Electronic pH-meter type 820. Spectrophotometric measurements were made with Pye-Unicam spectrophotometer SP8-100.

Chemically modified surface was prepared by Murray's procedure[5] Ti-strip (2×2 cm^2) was heated over oxidising flame for 20 minutes to get TiO_2 layer having characteristic lustre. Prior to silanization, electrode was polished, etched with 0.3 MHNO_3 + 5% HF solution for about 10 minutes and dried at room temperature. Metal oxide surface was allowed to stand at room temperature with 10% trimethoxyvinyl silane in anhydrous toluene (for 5 minutes). Finally surface was washed with fresh solution of toluene and air dried. Scanning electron microscope Model S-510 Hitachi (Japan) was employed for characterising a portion of modified surface, using an accelerating voltage 25KV, magnification x200.

Crude electrolyzed mixture obtained at C and modified electrode was evaporated under reduced pressure and residue dissolved in ether. Ethereal solution was treated with sodium carbonate solution and dried. Phenylacetic acid was recovered from alkaline extract by adding a few drops of dil. HCl. Ethereal solution was evaporated and residue on distillation gave benzylacetate. A portion was utilized to isolate dibenzyl by the procedure as follows. Ether extract of electrolyzed products obtained from oxidation of phenylacetic acid at Pt was distilled at 80–85° using water suction pump to remove voltatile substances. Residue was dissolved in hexane and dibenzyl isolated by column chromatography using silica gel. A portion was used up for isolation of ester as above. Chemical yield obtained at various electrodes (Table 1) has been calculated by ratio of actual yield/theoretical yield times 100.

TABLE I

% PRODUCT DISTRIBUTION AS FUNCTION OF ANODE-YIELDS ARE BASED ON MOLE PER CENT OF ORGANIC PRODUCT. 0.1M PHENYLACETIC ACID IN CH_3COOH/CH_3COOK, pH 5.2, TEMP. 22±1.0°C

Product	Gauze Pt	Amorphous carbon	Modified surface
Benzylacetate	13–14	70	63
Dibenzyl	67	<1	4–5

RESULTS AND DISCUSSION

Examination of electron micrograph depicts the image of light and dark regions, which correspond to raised and lowered features on the specimen Ti/TiO_2 surface due to etching treatment (vide Fig. 1(a)). Silanization resulted in no precipitate, dislocation and stacking fault structure on film Fig. 1(b); Fig. 1(c) is similar to Fig. 1(b) excepting certain line patterns of thick crystals and diminished contrast emerged. Fig. 1(d) projects only a modified view of F'g. 1(a) and Fig. 1(b). Nevertheless the specimen of chemically modified electrode is remarkably sturdy and retained its properties.

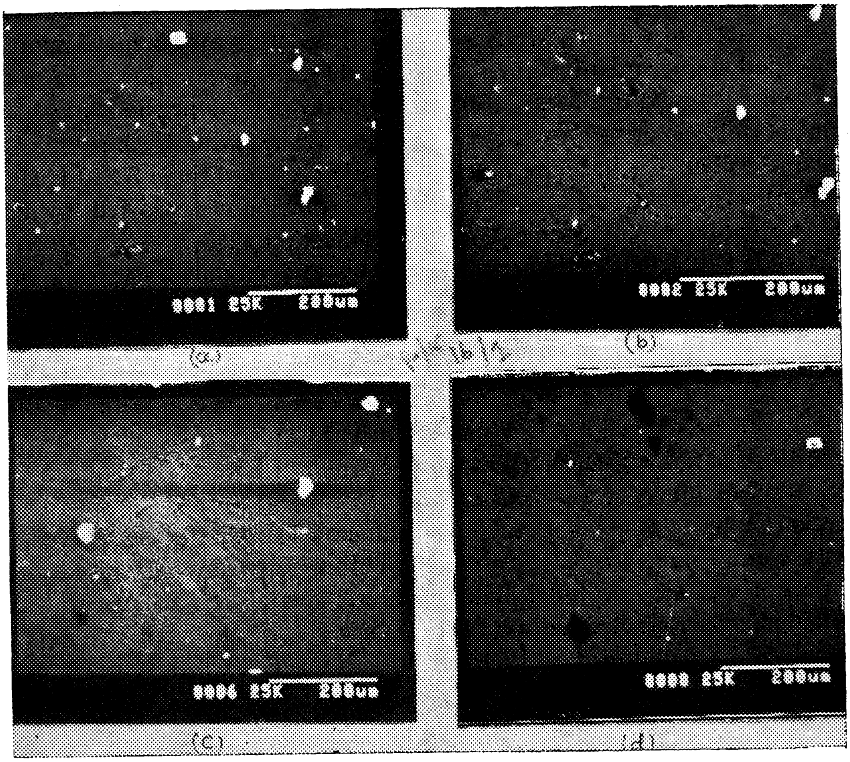

Fig. 1. Scanning electron micrographs of :
(a) Bare Ti/TiO_2
(b) Silanized Ti/TiO_2 surface before electrolysis
(c) Silanized Ti/TiO_2 surface immediately after electrolysis
(d) 24 hr. after electrolysis. Working distance 200 um.

Oxidation of phenylacetic acid at anodic potential of 1.85V, controlled potentiostatically, yielded a liquid product which on purification with 50% ethanol gave a good smelling, colourless liquid, $d_4^{22} = 1.062$. Analyses of sample revealed sharp λ_{max} (C_2H_5OH) at 340 nm, $n_D^{22} = 1.496$, C = 72.2% H = 6.7% and boils at 214-218°. These properties resemble that of benzylacetete and compares reasonably well with authentic (Aldrich) sample. However, oxidation of phenylacetic acid at Pt electrode under similar conditions yielded dibenzyl. After recrystallization from methanol gave monoclinic prisms having m. pt. 49-50°, C = 92.3%, H = 7.7%, $d_4^{22} = 0.987$ and peak λ_{max} (dioxane) = 272 nm which is contrary to the properties of the products obtained at other two electrodes. The sample showed similar properties with authentic dibenzyl (Aldrich) excepting that UV-spectrum resulted in 2 peaks at 265 nm and 288 nm instead of one.

Selection of anodic potential (1.85 V) is based upon certain preliminary studies[6] and its maintenance affects the elimination of oxidation of acetate which could have resulted in complexity of reaction sequence adversely due to side product formation.

Number of electrons consumed during oxidation of phenylacetic acid in CH_3COOH/CH_3COOK at pH 5.2 was determined by controlled potential coulometry. Measurement of decrease in concentration of electroactive compound with time and integration of the current consumed in electrolysis made it possible to calculate the involvement of number of electrons n = 2.

Temperature dependence and activation energy of process

Recently it was observed by Gupta and Raina[7] that increase in temperature did not affect the oxidation pattern of phenylacetic acid in the range 10°–35° in acetonitrile. Similar regularity was observed in case of phenylacetic acid when temperature was varied from 12–32°. Standard free energy change of activation Δ_G^* was thus obtained from relation[8] by plotting log i vs. 1/T in a potential range of about 90% of wave. Thus chemically modified surface revealed $\Delta_G^* = 43.5$ KJ mol^{-1} whereas values of 40.2 KJ mol^{-1} and 41.9 KJ mol^{-1} were obtained in case of carbon and Pt gauze anodes, respectively. This means surface tries to lower overpotential by enhancing both reaction rate and reaction selectivity[9].

Cyclic Voltammetry

Cyclic voltammetry of phenylacetic acid (1×10^{-3} M) in CH_3COOH/CH_3COOK at pH 5.2 using aforesaid microelectrode ($A \simeq 0.42$ cm^2), illustrates the following diagnostic features (*i*) a single anodic peak $E_p = 1.7$ V with no counter cathode peak on reverse scan at sweep rate 0.1–1 Vs^{-1}. A similar observation has been reported by Gupta and Raina[10] in case of diazaphenanthrene, (*ii*) E_p shows anodic shift as sweep rate increases, (*iii*) peak current i_p proportional to concentration of electroactive material and $v^{1/2}$ and (*iv*) constancy in current function

$i_p/cv^{1/2}$. These observations revealed the process as diffusion controlled and totally irreversible.

Presence of intermediate dibenzyl radical formed during electrode reaction has been proposed from the appearance of additional small anodic peak[11] at a sweep rate = 1.5 Vs^{-1}.

Electrode Mechanism

Oxidation of phenylacetic acid in CH_3COOH/CH_3COOK follows reaction sequence.

$$\text{(a)}\quad C_6H_5CH_2COO^- \longrightarrow C_6H_5CH_2COO^{\cdot} + e$$

$$\text{(b)}\quad C_6H_5CH_2COO^{\cdot} \longrightarrow C_6H_5CH_2^{\cdot} + CO_2$$

$$\text{(c)}\quad C_6H_5CH_2^{\cdot} \quad \begin{array}{l} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \\ \searrow C_6H_5CH_2^{+} + e \end{array}$$

$$\text{(d)}\quad C_6H_5CH_2^{+} + CH_3COO^- \longrightarrow C_6H_5CH_2OCOCH_3$$

During electrolysis anionic form of phenylacetic acid was maintained by adjusting pH 5.2 (pK 4.3). $C_6H_5CH_2COO^-$ ion undergoes an initial electron transfer to result in benzyl radical with evolution of CO_2. The former dimerizes conveniently on Pt surface resulting in dibenzyl (a conventional Kolbe product[12]). Benzyl radical is likely to undergo a further deelectronation reaction to benzyl cation. The cation formation is justifiable under substantially high electrolysis potential as intermediate benzyl radical has lower ionization potential (7.76 eV)[13].

Dissimilarity in % yield of reduction products can be ascribed to difference in electrode surface morphology and its kind. It has been observed that Pt gauze electrode surfaces favour certain reactions *e.g.*, Kolbe coupling product is major product (5 times higher compared with the yield of ester). On the contrary yield of ester is higher on amorphous carbon and modified surface (Table 1), while very little coupling product was observed. The favour of coupling product formation on Pt surface can be explained from the viewpoint that radical generated largely gets desorbed from the surface with elimination of CO_2. This step is followed by homogeneous chemical dimerization to dibenzyl.

Amorphous carbon surfaces impede desorption tendency[3] of radicals by exercising the available additional binding forces (paramagnetic centres residing on carbon) to attach bulk of generated radicals to electrode surface thus disfavouring radical coupling reaction. These radicals under the influence of applied electric field follow further deelectronation to cation. Benzyl cations being reactive towards nucleophilic attack of acetate ion, readily form benzylacetate.

Chemically modified electrodes[14] are known to enhance chemical microstructures capable of conferring selectivity and electrolytic properties to electrode. The electrocatalytic activity of electrodes and mechanism therein depend upon various factors relevant to physical and chemical nature of the film[15]. Primarily silanized Ti/TiO_2 surface seems to have lowered the overpotential of electrode reaction which might have provided necessary energy for ester formation. It can be concluded that spongy (or high surface) electrodes facilitate cation formation and further ester formation due to substantially low current density.

In other words electrodes are in general specific electrocatalysts for a given reaction and at appropriately chosen potential, a specific electronation or protonation rate can affect chemical environment as a whole.

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