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PHOTOELECTROCHEMICAL SYNTHESIS WITH PT-COATED TiO_2 POWDER: ALKYLATION OF 1-ALKYLPYRIDINIUM ION

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Abstract- A photoelectrochemical approach to the alkylation of 1-alkylpyridinium ion is described. Photolysis of a suspension of Pt-coated TiO_2 (anatase) powder in an aqueous medium containing isobutyric acid and 1-ethylpyridinium perchlorate (pH 3-4) yielded 4-isopropyl-1-ethylpyridinium ion. Seventy percent of the isopropyl radicals generated at the TiO_2 anode sites by the photo-Kolbe process were found to have alkylated 1-ethylpyridinium ion, in the 4-position, with the remaining 30% being reduced to propane.

Pt-coated TiO_2 powder dispersed in solution provides millions of microscopic photoelectrochemical cells.[3,4] A unique feature of these electrochemical cells is the size and arrangement of the anode and cathode sites such that a reactive product from the anodic process can combine with a reactive product from the cathodic process before they each undergo their own follow-up reaction. The work of Kraeutler and Bard on the photo-Kolbe reaction with n-TiO_2 semiconductor anode/Pt cathode electrochemical cells first called attention to this unique feature of the miniature electrochemical cells on the surface of Pt-coated TiO_2 powder particles.[3,4] They reported that the photolysis of a suspension of Pt-coated TiO_2 in an acetic acid/acetate solution produced methane and carbon dioxide, whereas in a conventional divided compartment cell containing acetate solution, photolysis of the TiO_2 anode produces ethane, hydrogen, and carbon dioxide.[5] The difference in photolysis products can be viewed as resulting from the coupling of the intermediates $CH_3\cdot$ and $H\cdot$ (produced at the anode and cathode, respectively) in the former case and from their dimerization in the latter.

In this paper, we demonstrate further the special utility of these miniaturized photoelectrochemical cells in synthesis.[6] We describe the ring alkylation of a 1-alkylpyridinium ion by the photolysis of a suspension of Pt-coated TiO_2 powder in a solution containing isobutyric acid and 1-ethylpyridinium(**1**) perchlorate. The photo-Kolbe process at the TiO_2 sites produced isopropyl radicals which combined with the 1-ethylpyridinyl radicals(**2**) formed at the Pt sites. The resulting dihydropyridine species, the 1,4-isomer(**3**), subsequently underwent oxidation at the TiO_2 anode sites to 4-isopropyl-1-ethylpyridinium(**4**) ion.[7]

RESULTS

Typical quantitative information on the products found in a 9-h photolysis of a mixture of 15 mg 6% Pt-TiO_2 and 15 mL of a 1.1 M isobutyric acid, 0.10 M 1-ethylpyridinium perchlorate solution, pH 3.8, is presented in Table I. The radiation source was a 300-W Xe lamp. The formation of **4** ion, the product of interest, was established by voltammetry (Figure 1) and ^1H NMR. Curve (a) is the voltammogram of the methylene chloride extract of a reaction mixture of 25 mg of 7% Pt-coated TiO_2 in 25 mL of a pH 3.4 solution 5 M in isobutyric acid and 0.5 M in **1** perchlorate before photolysis (attributable to **1** ion[8]) and curve (b) after 9-h photolysis and alkalification to pH > 12.5. The additional set of peaks in curve (b) suggested that another pyridinium species was present in solution. Addition of **4** iodide to the voltammetric solution for curve (b) indicated that the second cathodic peak and the first of the two small anodic peaks appearing in the reverse potential scan were attributable to the presence of the 4 ion. Further definitive information on the nature of this product was provided by a ^{1}H NMR

Table I. Data for a Typical 9-h Photolysis of 15 mL of Solution (1.1 F Isobutyric Acid, 0.10 F 1-Ethylpyridinium Perchlorate, pH 3.8) Mixed With 15 mg 6% Pt-TiO$_2$.

Products	mmoles	meq oxid	meq red
Carbon dioxide	0.98	0.98	---
4 ion	0.70	1.40	0.70
n-Propane	0.42	---	0.42
2,3-Dimethylbutane	small[a]	---	---
Hydrogen	small[a]	---	---
5[b] and 6[c]	0.17	---	1.02
Totals	---	2.38	2.14

[a] Less than 1% of mmoles of CO$_2$. [b] 1-Ethylpiperidine.
[c] 4-Isopropyl-1-ethylpiperidine.

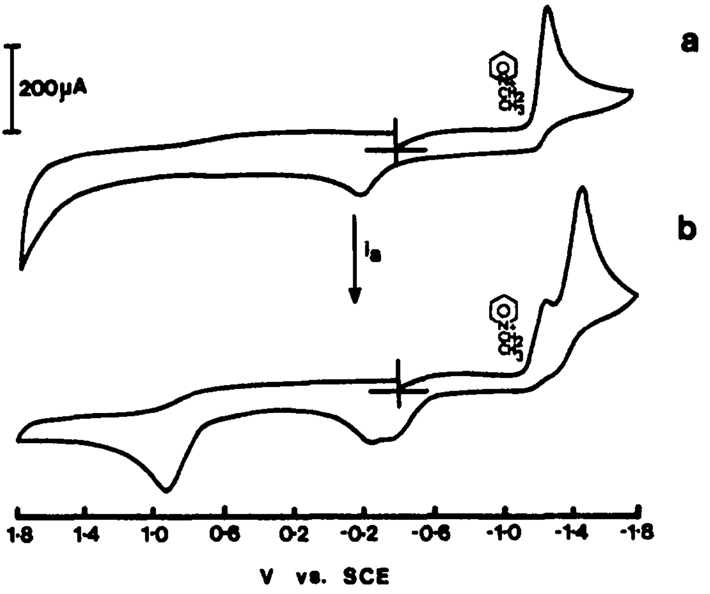


Figure 1. Cyclic voltammograms of methylene chloride extracts of the reaction mixture (a) before photolysis and (b) after 8 h of photolysis: 0.1 F TBAP, glassy carbon electrode, and 100 mV/s scan rate.

examination. For this study, we examined the residue obtained from evaporation of a base and acid washed sample of the methylene chloride extract of a reaction mixture after photolysis and alkalification. Washings with 0.1 M removed selectively the more water soluble 1 perchlorate from the new pyridinium species, as shown by voltammetry, and also residual isobutyric acid. Amine side products were removed by the acid washings with 0.1 M HCl solution. The ^{1}H NMR spectral data indicate that only the 4-substituted 1-ethylpyridinium species was formed in the photolysis. The data for the residue show that the triplet at 8.44 ppm for the ring hydrogen in the 4-position of 1 ion is absent; the triplet at 8.0 ppm for the ring hydrogen in the 3-position of 1 switches to a doublet; the doublet signal of the hydrogens in the 2-position at 8.8 ppm is still present; and a new doublet and multiplet appear at 1.3 ppm and 3.0 ppm, respectively, attributable to the isopropyl group.[9] The amount of 4 produced was determined by HPLC.

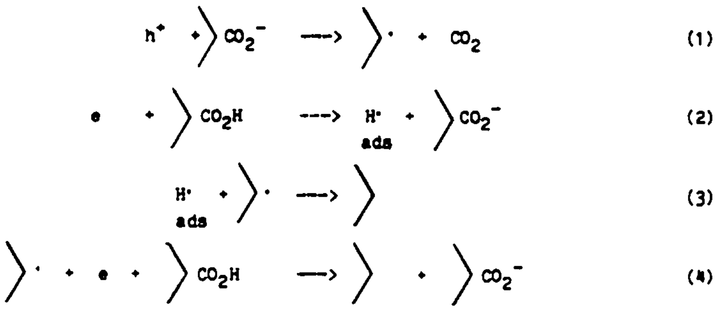
The gases propane and carbon dioxide were identified by GC-MS. The formation of a hexane isomer was revealed by the GC-MS data [m/e: 86 (M^+), 85, 71, 56]. The hexane isomer is undoubtedly 2,3-dimethylbutane (mass 86), the direct coupling product of two isopropyl radicals. Because it was not a major product, no attempt was made to examine the material in detail. GC data also indicated the presence of hydrogen. Quantitative work on these products were obtained by GC.

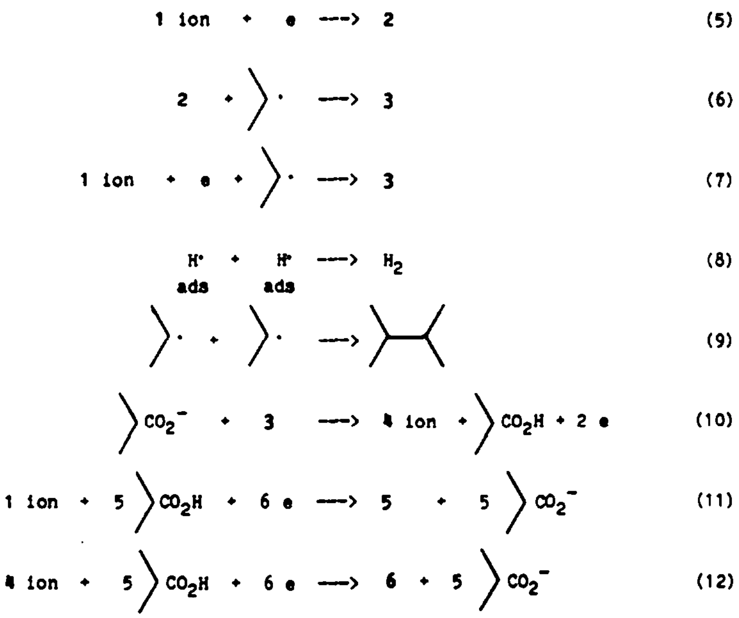
The formation of the small amount of piperidine compounds 5 and 6 was established by voltammetry, mass spectrometry, and ^{1}H NMR spectroscopy. (Details of these studies are presented in the EXPERIMENTAL section.) The two piperidine species were quantified as a single species by spiking the sample used in the voltammetric study of 4 ion formation (Figure 1,b) with a known amount of piperidine. The seemingly large amount of piperidine formation suggested by the magnitude of the anodic peak at +1.0 V in curve (b) is the results of the highly selective partitioning of the piperidine species into the methylene chloride phase. Based on the mmoles of 1 ion taken originally and the amount of 4 ion formed, the ratio of 6 to 5 should be less than one.

From the mass balance of carbon dioxide to products containing the isopropyl group (0.98 mmoles to 1.12 mmoles) and the agreement of total meq of oxidation process to meq of all reduction processes (2.38 meq to 2.14 meq), it can be concluded that the key products of the photolysis process have been accounted for.

In the examination of reaction parameters two things are noteworthy. Pt loading is essential. On photolysis of 15 mL of an aqueous reaction mixture (1.1 M in isobutyric acid, 0.10 M in 1 perchlorate, and pH of 4) containing 15 mg of Pt-TiO_2 powder, without Pt coating only traces of gas and 4 ion were detected; at 0.7% Pt loading, the rate of CO_2 evolution was 1.6 umoles/min; and at 6 % loading, increased to 2.4 umoles/min. pH is the other important consideration. At pH's higer than 5 and lower than 2, the amounts of products were minimal, a situation similar to that observed with acetate medium.[2]

With the information we have obtained and the consideration of a scheme proposed for similar photolysis with acetic acid/acetate solution[4], the following mechanistic scheme is offered:





Equations 3 and 4, and 6 and 7 are of particular importance because they describe reactions between reactive anodic and cathodic intermediate products. The electrode process described in Eq (7) can shift the reduction of 1 ion from its voltammetric potential of -1.4 V to a more positive potential.

DISCUSSION

This study has shown that the preparation of ring alkylated 1-alkylpyridinium ion can be easily accomplished by photolysis of Pt-coated commercial TiO_2(anatase) powder suspended in an alkylcarboxylic acid/1-alkylpyridinium perchlorate solution. With isobutyric acid/1-ethylpyridinium perchlorate solution (pH 3-4), the ring alkylated product (the 4 isopropyl substituted pyridinium species) accounted for 70% of the photogenerated alkyl radical, with propane accounting for the remaining 30%.

The photoplatinization of TiO_2 powder in an acetate medium containing chloroplatinic acid appears to produce small islands of Pt highly dispersed on the surface of the TiO_2 particles. The small amounts of hydrogen gas and 2,3-dimethylbutane that have been obtained in the photolysis studies with isobutyric acid/isobutyrate solutions indicate that there is an because of the large surface area of the powder. Furthermore, with the vast number of microscopic sites of Pt and TiO_2, each alkyl radical is surrounded by more of the pyridinyl radical and hydrogen atom than by its own kind and vice versa. Dimerization is, therefore, minimal and the chance of cross coupling is high. The need for platinization of the n-TiO_2 powder to make possible the photoelectrochemical action indicates that the cathodic electron-transfer processes have less overvoltage on Pt than on a TiO_2 surface.[3,4,10,11] The absence of hydrogen gas formation with platinized anatase in our isobutyric acid/isobutyrate solutions indicates no build up of $H^{\cdot}_{ads}$, which is consistent with its rapid uptake by a photogenerated alkyl radical. Details of this photoelectrochemical process are currently under study.

EXPERIMENTAL

Materials. The solvents diethyl ether, methanol (anhydrous, Mallinkrodt), ethanol (anhydrous, Fisher Scientific Co.), methylene chloride, and pentane were reagent grade. Acetonitrile was HPLC grade material (Fisher Scientific Co.).

Reagent grade chemicals titanium dioxide (TiO_2, anatase powder, Matheson Coleman and Bell), chloroplatinic acid (Aldrich Chemical Co.), sodium acetate, sodium hydroxide, potassium hydroxide, sodium perchlorate, lithium perchlorate, tetraethylammonium perchlorate (TEAP, Eastman Organic Chemicals), and hydrochloric acid were used as obtained. Tetrabutylammonium perchlorate (TBAP, Eastman Organic Chemicals) was examined by voltammetry and purified when necessary. TEAP was similarly examined. Purification of TBAP involved dissolution in reagent grade acetone, filtration of the resulting mixture to remove debris in the salt, and treatment with water to precipitate the perchlorate salt. The crystals were dried overnight in a vacuum oven and stored in a desiccator.

Platinized TiO_2 powder (6% by weight) was prepared according to a procedure described earlier.[12] In our slightly modified version of the procedure, hexahydrated chloroplatinic acid (0.208 g) and titanium dioxide powder were added to 2000 mL of an acetic acid/acetate solution containing 81.5 g of sodium acetate and 680 mL of glacial acetic acid. The mixture was deoxygenated with nitrogen and directly photolyzed with a 300-W Xe lamp for 10 h while being stirred. Radiation from the lamp and heat from a hot plate were used to maintain the temperature of the solution at 55°C. After irradiation, the mixture was transfered to a beaker and the platinized TiO_2 particles allowed to settle. The clear colorless supernate was decanted and the Pt-TiO_2 was washed three times with distilled water and dried overnight at 110°C.

The organic compounds glacial acetic acid, pyridine, ethyl iodide (Aldrich Chemical Co.), isobutyric acid (Matheson Coleman and Bell), 1-ethylpiperidine (97% Aldrich Chemical Co.), 4-isopropylpyridine (Columbia Organic Chemical Co.) were reagent grade or the highest purity available.

1-Ethylpyridinium(1) perchlorate. The 1 iodide was prepared following the methods reported in the literature.[13] The conversion of this salt to the perchlorate compound was carried out by precipitation from a methanol solution (40 mL) of 1 iodide (20 g, 0.09 mole) and lithium perchlorate (9 g 0.09 mole) by dropwise addition of ethyl ether. This precipitation procedure was repeated until iodide was not detected in the product by voltammetry. The salt was finally recrystallized from methanol (with no lithium perchlorate present) as described above.

4-Isopropyl-1-ethyl-pyridinium(4) iodide. This pyridinium salt was prepared according to the procedure described by Kosower et al.[13b] ^1H NMR (80 MHz, $CDCl_3$), 1.35 (d, $[CH_3]_2$), 1.70 (t, $-CH_3$), 4.65 (q, $N-CH_2-$), 7.85 (d, $H_{3,5}$), 8.75 (d, $H_{2,6}$). *Anal*. Calcd for $C_{10}H_{16}NI$: C, 43.33; H, 5.82; N, 5.05. Found: C, 42.58; H, 5.40; N, 5.18.

4-Methyl-1-ethyl-1,4-dihydropyridine(3a). This compound was prepared by the method of de Koning et al.[14] The product was stored under argon at -20° C: MS (EI) m/e (relative intensity): 123 (M^+, 20%), 108 (100%), 94 (20%), 80 (20%), 65 (5%), 53 (15%); ^1H NMR (80 MHz, $CDCl_3$), 5.69 (d, $H_{2,6}$), 4.32 (q, $H_{3,5}$), 3.0 (m, H_4 and CH_2). Potential for oxidation: $E_{1/2}$ vs SCE = +0.30 V (acetonitrile, 0.1 *F* TEAP, glassy carbon electrode).

Tetrabutylammonium isobutyrate. Preparation of this salt involved the slow addition of isobutyric acid (50 mmoles, 4.2 mL) to 50 ml of a methanol solution 1 *F* in tetrabutylammonium hydroxide. The product was dried in a vacuum oven at 60° for 7 days and stored in a desiccator over P_2O_5.[5]

Instruments. ^1H NMR measurement was made on one of three spectrometers: A 300-MHz Varian XL-300, a Varian Anaspect EM-360, and a 80 MHz Varian FT80. Mass spectrometric work was performed on a Varian CH5 spectrometer and a Nermag R10-10 quadrupole mass spectrometer (a DB-1701 capillary column and a probe injection system were available). A Matheson Dual Column gas chromatograph model 8430 equipped with a thermal conductivity detector and a Varian Aerograph Series 1800 Dual Column chromatograph with flame ionization detection were used. An integration system of our own design was attached to the Matheson unit, and a Zenith Data System Z-100 computer-controlled voltage to frequency converter employing Microsoft Z-Basic (Z-DOSTM)[15] was coupled to the Aerograph unit. A Spectra Physics Model 8P8700 liquid chromatograph with 254 nm detection (using either a LDC-UV monitor 1250 or a DuPont Model 840 LC detector) was utilized for HPLC. Chromatograms were recorded with a Linear 1100 recorder and peak heights were read off a Simpson Model 464 digital multimeter. The signals from the detector were amplified by a laboratory designed unit. Equipment for electrochemical studies has been recently described.[16] A 0.6-cm diameter glassy carabon electrode (Princeton Applied Research) was employed as the working electrode. Argon was used to deaerate the solutions for electrochemical study and to maintain an inert atmosphere over the solution during voltammetric measurement.

Photolysis. The apparatus for the photolysis experiments was a slightly modified version of that described by Kraeutler and Bard.[4] Our light source was a 300-W Xe lamp (EIMAC division of Varian). The radiation from the lamp was passed through 7 cm of water in a Kimax dish. The sample was placed in a square Vycor cell 1" x 1". In a typical run, 15 mL of the photolysis solution and 15 mg of the Pt-TiO_2 powder, along with a stirring bar, were placed in the sample cell, and helium was passed through the mixture via a bubbling tube sealed into the cell. After 10 min, a gas venting valve located between the gas buret and the cell was closed and as the mercury level in the gas buret slowly dropped, the pressure inside of the apparatus was equalized with that outside by lowering the leveling bulb. When the gas buret was filled, the stopcock serving as the gas vent was opened and the mercury level was slowly raised. This process was repeated at least eight times to purge the apparatus of oxygen. Complete removal of oxygen by this procedure was confirmed by gas chromatography. For the photolysis, the water jacket was maintained at 55±5°C. During the course of the photolysis, the pressures inside the cell and that outside were equalized periodically. After the photolysis, 1.00 mL samples of gas were removed for chromatographic analysis.

Separation and Quantification of **4** *Ion*. The HPLC procedure involved taking an aliquot of a diluted sample of the reaction mixture after photolysis and separating the product from **1** ion ion by passage through a 25 cm x 4.6 mm bare (unbonded) silica, 8 um, column coupled with a mobil phase of 70v/% acetonitrile, 30v/% water, 20 mM $NaNO_3$ and 2 mM $NH_4H_2H_2PO_4$[17] and 250 nm detection.

Gas Analysis. The gaseous products carbon dioxide and propane were separated and determined with a 1/4" x 6 ' Porapak-Q column mounted on the Matheson gas chromatograph. The column was set at a temperature of 160°C. Hydrogen and oxygen were analyzed separately by chromatography with a 1/4" x 5' molecular sieve column maintained at room temperature and mounted on the same chromatograph. The column required overnight purging with helium at 250°C. 2,3-Dimethylbutane was determined by gas chromatography utilizing a 1/8 x 10', 5% SE-30 on Chromasorb W column (at 70°C) attached to the Varian gas chromatograph. Toluene was used as the solvent to introduce 2,3-dimethylbutane for calibration. The removal of the toluene required an increase in the column temperature to 190°C. The quantities of O_2, H_2, and 2,3-dimethylbutane found were each less than 1 % of the amount of CO_2. Helium was the carrier gas in all the gas chromatography work.

Identification of 5 and 6. From the acid-base effect observed on the extractability of the material responsible for the prominent anodic peak at +1.0 V in the cyclic voltammogram for the methylene chloride extract of the reaction mixture after photolysis and alkalification (Figure 1b), the presence of an amine product in the reaction mixture was suspected. 5 and 6 were isolated by treating the methylene chloride extract with aqueous 0.1 *M* HCl solution, making the aqueous phase basic, and extracting with methylene chloride. A uL portion of this methylene chloride solution was placed on the mass spectrometer probe and the probe temperature was slowly increased. The presence of two substances close in boiling point was noted. 5 and 6 account for the resulting mass spectrum of m/e: 155, 154, 140, 126, 113, 112, and 98. 6 has a mass of 155 and 5 a mass of 113.

The ^{1}H NMR spectrum of the residue from the mass spectral work has the three principal signals for the ^{1}H's in 5: the methylene hydrogens adjacent to the nitrogen (2.4 ppm), the remaining ring hydrogens (1.1-2.0 ppm), and the methyl hydrogens (1.0 ppm). In addition, the spectrum has additional features which can be attributed to the presence of the 4-substituted derivative: a doublet at 0.9 ppm for the methyl hydrogens of the isopropyl group and a change in the 1.1-2.0 ppm ring hydrogen signals.

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