Attachment of Permethylpolysilane Groups to Platinum by Electroreduction of Chloropermethylpolysilanes. X-Ray Photoelectron Spectroscopy of Permethylpolysilanes Chemically Bound to Electrode Surfaces

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Abstract: Permethylpolysilane groups have been bonded covalently to platinum electrodes by electrochemical reduction of chloropermethylpolysilanes in acetonitrile. The permethylpolysilanes were observed by x-ray photoelectron spectroscopy of the platinum electrode surface. From cyclic voltammetry, the ferrocene/ferrocenium couple is less reversible (slower electron transfer) at an electrode having bound permethylpolysilyl groups than at an untreated normal platinum electrode. In controlled-potential electrolysis, chlorotrimethylsilane gave hexamethyldisiloxane as the only silicon-containing product at both the cathode and anode when tetra-*n*-butylammonium perchlorate was used as the supporting electrolyte. When tetra-*n*-butylammonium chloride was used as the supporting electrolyte, hexamethyldisilane was the only silicon-containing product at both the cathode and anode.

Introduction

The cyclic voltammogram of chlorotrimethylsilane is consistent with a one-electron quasi-reversible reduction[1] and thus implies the formation of the chlorotrimethylsilyl anion radical. However, our attempts to observe the anion radical by electron spin resonance were unsuccessful. The absence of an ESR signal could be attributed to adsorption of the radical onto the platinum working electrode. Therefore, this study was undertaken for the purpose of searching for permethylpolysilanes adsorbed on, or bound to, platinum electrodes. As a part of this study, the electrolysis products of chlorotrimethylsilane at the cathode and anode were determined. Lane and Hubbard[2] described the strong chemisorption of electroactive allyl compounds onto platinum electrodes, and, after this work was started, several reports on compounds covalently bonded to electrode surfaces have appeared. Organic ligands, including organosiloxyl groups, have been bound by chemical reactions to the surfaces of graphite and metal oxide electrodes.[3] Carbon, metal oxide, and platinum electrodes have been chemically modified with a variety of reagents including one or more of the following: aminopropyltriethoxysilane,[3a,f] (*S*)-(−)-phenylalanine methyl ester (giving chiral centers on the electrode),[3b,3d] a 4-arylazo-1-naphthol derivative,[3c] β-trichlorosilyl(2-ethyl)pyridine,[3e] [(CH$_3$O)$_3$Si(CH$_2$)$_3$SH/Fe$_4$S$_4$(*t*-BuS)$_4$]$^{2-}$,[3g] porphyrins,[3h,k] 3-(2-aminoethylamino)propyltrimethoxysilane/3,5-dinitrobenzoyl chloride,[3i,j] and 3-(2-aminoethylamino)propyltrimethoxysilane/*N*-anisylpyrazoline derivatives.[3l]

The main points of interest in this study were (1) the binding of polysilanes electrochemically to platinum electrodes, as determined by x-ray photoelectron spectroscopy (XPS); (2) the comparison of binding energies of the silicon 2p electrons in the products from the reduction of chlorotrimethylsilane and 1-chloroterdecamethylhexasilane; and (3) the testing of the electrochemical reversibility of the ferrocene/ferrocenium couple using an organosilicon-coated platinum electrode.

Experimental Section

Acetonitrile (Baker Analyzed reagent) was distilled over calcium hydride and phosphorus pentoxide and passed through a column of dry alumina prior to use. Tetra-*n*-butylammonium perchlorate (Southwestern Analytical Chemicals, Inc.) was recrystallized from ethanol, dried, and stored in a desiccator. Chlorotrimethylsilane (PCR, Inc.) was redistilled and stored in sealed ampules. Chloropermethylpolysilanes[1,4] and dodecamethyloxacycloheptasilane (alter-

native name: 2,2,3,3,4,4,5,5,6,6,7,7-dodecamethyl-1-oxa-2,3,4,5,6,7-hexasilacycloheptane)[5] were prepared by published methods. Ferrocene was recrystallized from cyclohexane, and tetra-*n*-butylammonium chloride (Eastman) was used without further purification.

Controlled-potential electrolyses and cyclic voltammetry were performed with equipment and by methods described elsewhere.[1] Solutions were 0.1 M in supporting electrolyte in acetonitrile, and the working, reference, and counter electrodes were platinum. The potentials reported in this work are referenced to a platinum reference electrode. The platinum reference electrode is assumed to be +0.6 V more positive than the saturated calomel electrode.[6]

In the electrolyses involving the preparation of organosilicon-coated electrodes, the working electrode, 1.1 by 0.4 cm, was first conditioned in the acetonitrile/tetra-*n*-butylammonium perchlorate solutions at a positive potential of +0.5 V for 1 min, followed by a negative potential of specified magnitude and duration. Throughout the electrolysis, the solution was stirred by bubbling in purified nitrogen. The working electrode was then washed with distilled water, dried at 60 °C, and analyzed by XPS within 24 h of the electrolysis.

An AEI ES-200 photoelectron spectrometer with a fixed instrumental resolution of 1% was utilized. Aluminum Kα radiation (1486.6 eV) was used as the photon source. The platinum working electrodes were mounted directly onto the XPS sample probe. The sample of dodecamethyloxacycloheptasilane was put on an aluminum strip and the XPS spectrum obtained at 0 °C. The spectra were calibrated using the Au(4f$_{7/2}$) electron line (84.0 eV). Under normal conditions, a gold reference sample yields a 4f$_{7/2}$ peak intensity of 4500 counts channel^{-1} s^{-1} with a fwhm of 1.3 eV. The work function of the spectrometer is 3.3 eV. Typical operating vacuum is 10^{-7} Torr. A PDP-8S computer is attached to the XPS unit for data acquisition.

After analysis by XPS, the sample electrodes were cleansed by immersion in hot (ca. 60 °C) concentrated nitric acid for 30 s, followed by electrochemical oxidation for 30 s in 1 M hydrochloric acid. With fresh solutions, the oxidation was repeated for another 30 s, followed by immersion in concentrated nitric acid for approximately 15 s, washing with distilled water, and drying at 110 °C. All solutions were continuously stirred.

Exhaustive electrolyses were done in a low-temperature, large-volume three-compartment preparative cell[6] which allowed separation of anode and cathode electrolysis products.

ESR scans at −25 °C were made with a Varian Associates Model E-4 spectrometer and a low-temperature electrochemical cell[6] while simultaneously electrolyzing 0.027 M solution of chlorotrimethylsilane in acetonitrile with 0.05 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte.

Results

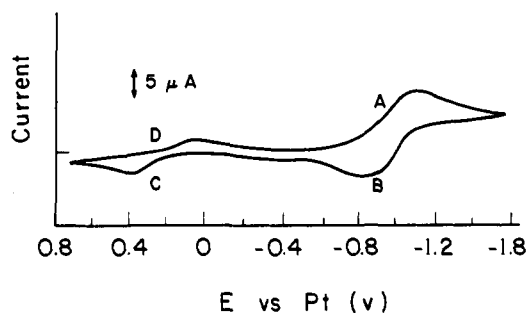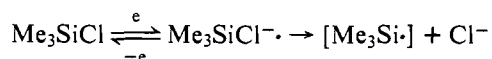**Electrolysis of Chlorotrimethylsilane.** Coulometry shows

Figure 1. Cyclic voltammogram of Me_3SiCl. (Scan rate, 0.42 V/s; 0.1 M tetra-n-butylammonium perchlorate is the supporting electrolyte.)

Figure 2. (A) XPS spectrum of the silicon 2s peak detected on a platinum electrode used in the reduction of $Me(SiMe_2)_6Cl$. (B) Background spectrum from untreated electrode.

that both oxidation and reduction of chlorotrimethylsilane requires 1 faraday/mol. For solutions containing 0.05 M chlorotrimethylsilane and 0.1 M tetra-n-butylammonium perchlorate in acetonitrile at −26 °C, oxidation (+1.5 V), with the final current less than 0.01 of the initial current, involved ∼0.95 faraday/mol and reduction (−1.5 V) involved ∼1.15 faradays/mole.

Analysis by NMR revealed that the products of electrolysis were different with different supporting electrolytes. With tetra-n-butylammonium chloride as the supporting electrolyte, hexamethyldisilane is the only silicon-containing product at the cathode *and* the anode. The final solution in the anode compartment has residual oxidizing power as demonstrated by the color of iodine following the addition of tetra-n-butyl-ammonium iodide. With tetra-n-butylammonium perchlorate as the supporting electrolyte, hexamethyldisiloxane, but no other silicon-containing compound, is produced in *both* electrochemical oxidation and reduction. The electrolysis of chlorotrimethylsilane at 75 V with a mercury anode and lead cathode in 1,2-dimethoxyethane containing $[(n\text{-Bu})_4N]ClO_4$ as the supporting electrolyte has been reported[7] to give hexamethyldisilane.

The pattern of products in the anode and the cathode compartments with different supporting electrolytes is consistent with common intermediates, such as Me_3SiCl^- or Me_3SiCl^+, followed by reaction of these intermediates or more likely their decomposition products with any perchlorate ion present.

Cyclic Voltammetry and ESR. The cyclic voltammogram, Figure 1, of chlorotrimethylsilane exhibits a wave (A) attributable to quasi-reversible formation of the anion radical, $Me_3SiCl^-\cdot$, as reported earlier.[1] The reoxidation wave (B) is broader than the reduction wave (A) and does not appear to any great extent unless the electrodes are electrochemically conditioned, generally at +0.5 V for ca. 5 min. Stirring the solution by bubbling nitrogen gas into the solution prior to obtaining a subsequent cyclic voltammogram causes a decrease in the magnitude of the reoxidation current. With decreasing scan rate, wave C decreases faster than wave A. Waves C and D are not present in an initial cyclic scan from zero to positive potentials with tetra-n-butylammonium perchlorate as the supporting electrolyte. With only tetra-n-butylammonium chloride in acetonitrile, waves at C and D appear. Therefore, in the cyclic voltammetry of Me_3SiCl, waves C and D are a consequence of the chloride ion which is produced in the coupled chemical reaction:

$$Me_3SiCl \underset{-e}{\overset{e}{\rightleftharpoons}} Me_3SiCl^-\cdot \rightarrow [Me_3Si\cdot] + Cl^-$$

In a cyclic voltammogram of chlorotrimethylsilane, a scan to −1.0 V followed by a pause for 10 s at 0 V on the reverse scan led to a decrease in wave C and the conclusion that wave C is not due to oxidation of $-SiMe_3$ bound to the electrode surface. The $Me_3Si\cdot$ radical, postulated above, should rapidly dimerize or react with either the solvent or supporting electrolyte.
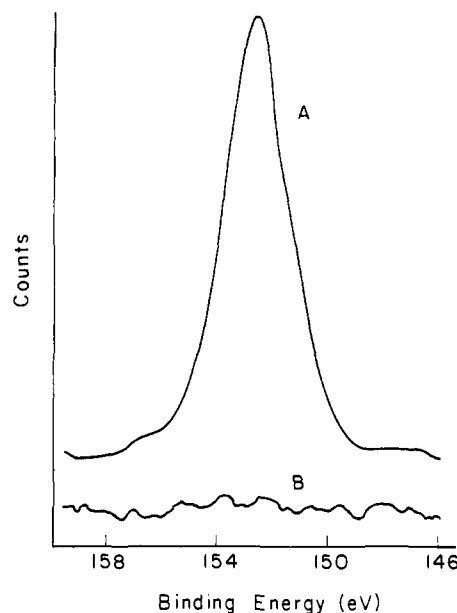
Since the half-life of the species, presumably $Me_3SiCl^-\cdot$, formed at wave A is at least a few seconds, ESR scans were taken while electrochemically reducing Me_3SiCl in a flow cell. However, no ESR signal was observable at 25 °C or at −25 °C. Speculation about $Me_3SiCl^-\cdot$ being adsorbed on the electrode surface led to the XPS experiments reported next.

X-Ray Photoelectron Spectroscopy. As described in the Experimental Section, platinum strips were pretreated, used as electrodes in the reduction of chlorotrimethylsilane, 1-chloroterdecamethylhexasilane, or 1,6-dichlorododecamethylhexasilane, washed, dried, and examined by XPS.

In this report, "background" electrodes refer to platinum strips used in acetonitrile/supporting electrolyte and "sample" electrodes refer to platinum strips used in acetonitrile/supporting electrolyte/organochlorosilanes. Figure 2 contains a typical XPS spectrum covering the Si(2s) region and showing a strong peak for the same electrode used to electrolyze 1-chloroterdecamethylhexasilane. Figure 3 shows full-scan XPS spectra (kinetic energy of 900–1400 eV) of background and sample electrodes from the electrolysis of 1,6-dichlorododecamethylhexasilane. These spectra are particularly instructive in that they show vast differences between background and sample electrodes. The spectrum of the background electrode shows intense peaks for the Pt(4d) and Pt(5s) regions, a small amount of oxygen probably due to platinum oxide, and a small carbon peak due to vacuum pump oil. The spectrum of the sample electrode shows a larger carbon peak (due to the methyl groups on the silicons), much smaller Pt(4d) peaks, the complete absence of the Pt(5s) peak, and the appearance of the Si(2s) and Si(2p) peaks. The decrease in the platinum photoelectron peak intensities, along with the observance of the silicon photoelectron peaks, indicates considerable coverage of the platinum surface with silicon. The large oxygen peak in this particular sample is due to addition of H_2O and more chlorosilane to the solution to form siloxane

$$[PtO\text{—}Si_6\text{—}(O\text{—}Si_6\text{—})_n Y]$$
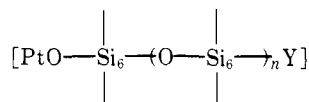
bound to the electrode. No XPS peaks due to chloride on this sample electrode or any other silicon-coated electrode were detected.

Table I. Experimental Binding Energies for Silicon 2s and 2p Electrons

	Si(2s)		Si(2p)	
	binding energy, eV[a]	no. of electrodes	binding energy, eV[a]	no. of electrodes
electrode treated with Me₃SiCl	152.9 ± 0.5	7	99.3 ± 0.1	3
electrode treated with Cl(SiMe₂)₆Cl	152.9 ± 0.4	8		
electrode treated with Me(SiMe₂)₆Cl	152.8 ± 0.1	5	99.7 ± 0.2	2
SiO₂	154.6[b]		103.2	
(SiMe₂)₆O	154		102.6	
Si	150.8		99.2[b]	

[a] Referenced to gold (84.0 eV for $4f_{7/2}$). Standard deviation stated. [b] Reference 8.

A platinum strip placed in a solution of chlorotrimethylsilane/tetra-*n*-butylammonium perchlorate in acetonitrile for 10 min but without applied potential exhibited no photoelectron peak for silicon. Thus, electroreduction, and not chemisorption or a chemical reaction, is responsible for silicon on the platinum surface.

For the three chlorosilanes used to coat platinum electrodes, the potentials and initial currents are −1.0 V and 0.6 mA for chlorotrimethylsilane, −0.95 V and 0.7 mA for 1,6-dichlorododecamethylhexasilane, and −0.70 V and 0.65 mA for chloroterdecamethylhexasilane. The Si(2s) and Si(2p) binding energies observed for the treated electrodes are presented in Table I. Also in Table I are collected binding energy data for pure dodecamethyloxacycloheptasilane, Si, and SiO₂. An attempt was made to resolve peaks due to nonequivalent silicon atoms on the surface of platinum which had been used to reduce 1,6-dichlorododecamethylhexasilane. Deconvolution of the resulting 2s peak was undertaken with a DS 100 data system (Digital Equipment Corp.), but no resolution of peaks due to silicon in differing environments was observed. Deconvolution of the 2s peak in dodecamethyloxacycloheptasilane was also attempted without success.

An electrode treated with chlorotrimethylsilane gave a silicon (2p) photoelectron binding energy which was slightly lower than, or equal to, that of an electrode treated with 1-chloroterdecamethylhexasilane. Equal Si(2s) binding energies, within experimental error, were observed for electrodes treated with the three chlorosilanes.

XPS peaks due to oxygen were detected on the surfaces of background electrodes and of electrodes treated with each of the chlorosilanes. The oxygen 1s binding energies (referenced to gold at 84.0 eV for $4f_{7/2}$) for a background electrode, an electrode treated with chlorotrimethylsilane, and of pure dodecamethyloxacycloheptasilane are 532.0, 532.2, and 533.4 eV, respectively; the corresponding oxygen 1s line widths are 4.5, 4.25 and 2.2 eV, respectively. The wide oxygen 1s line widths in the platinum electrode sample probably are due to a variety of oxygen-containing species on the electrode surface. An oxygen 1s binding energy of 531.8 eV has been reported[9] for PtO_ads prepared either by chemisorption of oxygen on a clean platinum surface or potentiostatically in 1 M HClO₄ at +0.7 V (vs. SCE) for 3 min. The photoelectron spectrum of a platinum background electrode in the Pt($4f_{7/2}$) and Pt($4f_{5/2}$) regions gave peaks with corrected binding energies of 71.5 and 74.8 eV, respectively, which are similar to the values reported by Kim, Winograd, and Davis[9] for PtO_ads.

On a typical platinum working electrode surface, a monolayer of trimethylsilyl groups would contain on the order of 10^{14} atoms of silicon. This amount of silicon should be electrochemically deposited from chlorotrimethylsilane in less than 1 s with a current of 0.1 mA if no other silicon-containing product formed. Experimentally, silicon from a chlorotrimethylsilane sample electrolyzed at −1.0 V for 3 s (0.6 mA) could be detected. An appreciable amount of silicon became bound to the platinum surface at a potential of only −0.466
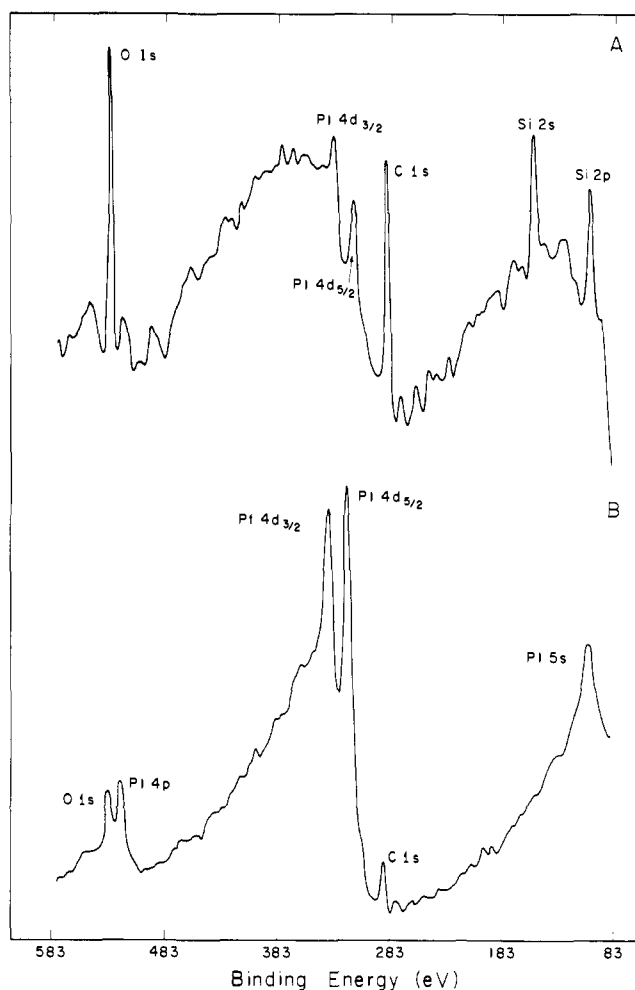

Figure 3. Full-scan XPS spectra of platinum electrodes: (A) sample strip used to electrolyze Cl(SiMe₂)₆Cl; (B) background spectrum from untreated electrode.

V during a 3-min electrolysis. Three-minute electrolyses at −1.0 V were done to ensure high sample counts for silicon.

Removal of Silicon from Platinum Surfaces. By recording x-ray photoelectron spectra of a silicon-coated platinum strip under identical conditions before and after the platinum strip served as the anode in an acetonitrile/tetra-*n*-butylammonium perchlorate solution, it was established that the bound organosilyl groups can be removed by electrochemical oxidation. With an applied potential of +0.90 V for 3 min, 65% of the silicon was removed from a platinum strip which had been coated with -SiMe₃ groups during an electroreduction of chlorotrimethylsilane. Likewise with an applied potential of +1.00 V for 3 min, 64% of the silicon was removed from an electrode which had been treated previously with 1,6-dichlorododecamethylhexasilane. During 19 h of electrolysis at

Table II. Peak Separations in Cyclic Voltammograms of $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ with Normal and Coated Electrodes

scan rate, V/s	normal electrode peak separation, mV	treated electrode peak separation, mV
0.090	75	85
0.18	78	97
1.8	188	240
7.8	357	424
13	456	707

+1.12 V, all silicon apparently was removed from an electrode which had been treated with 1,6-dichlorododecamethylhexasilane.

Silicon is not removed from organosilicon-coated electrodes by electrochemical reduction in acetonitrile/tetra-n-butylammonium perchlorate solutions. An applied potential of −1.25 V for 30 min did not cause a decrease in the intensity of XPS peaks due to silicon.

Electrodes coated with organosilyl groups could not be cleaned satisfactorily with concentrated nitric acid and rinsing. After treatment with nitric acid, the platinum strip was contaminated by SiO_2 as indicated by a Si(2p) photoelectron peak at 103.2 eV. The cleaning process described in the Experimental Section led to silicon-free surfaces.

Electrochemical Reversibility of the Ferrocene/Ferrocenium Couple at a Polysilane-Coated Electrode. For cyclic voltammetric experiments, a working electrode was treated by reducing 1-chloroterdecamethyltetrasilane at −1.0 V for 10 min, rinsed, and then immediately transferred to an acetonitrile solution containing 0.003 M ferrocene and 0.1 M tetra-n-butylammonium perchlorate. This permethylhexasilanyl-coated electrode and an untreated electrode of comparable small size were used in a series of cyclic voltammetric scans which are summarized in Table II. Clearly, coating the electrode with permethylhexasilanyl groups leads to slower rates of electron transfer or less electrochemical reversibility. Charge transfer rates are generally lower for chemically treated metal oxide and carbon electrodes than for untreated electrodes.[3a,f,h]

Cyclic voltammograms of ferrocene taken after oxidizing the coated electrode for 1 h at +1.5 V in acetonitrile containing tetra-n-butylammonium perchlorate were identical with those obtained with an untreated working electrode.

Discussion

Photoelectron spectra of the platinum working electrodes used in the reduction of chlorotrimethylsilane show that the trimethylsilyl group is chemically bound to the electrode surface. Chemisorption was ruled out as a possible cause of the results since a platinum strip in the absence of electrolysis but in contact with chlorotrimethylsilane in acetonitrile/supporting electrolyte gave no indication of a silicon XPS signal. Reduction of 1,6-dichlorododecamethylhexasilane and of 1-chloroterdecamethylhexasilane also resulted in silicon bound to the electrode surface. The silicon was difficult to remove from the electrode surface unless the electrode was electrochemically oxidized, indicating that the silicon is covalently bound to the platinum electrode. Moreover, the detection of silicon and oxygen on the sample electrode surface leads to the conclusion that the silyl groups are chemically bound to platinum through oxide bridges. The surface species, $PtO-SiMe_3$, is inferred from the oxygen (1s) binding energy.

The measured binding energies of silicon in the samples falls between those of pure silicon and of silica. The silicon (2s) binding energies of electrodes treated with the three chlorosilanes studied are essentially the same. The silicon (2p) binding energy for the electrode treated with chlorotrimethylsilane is 0.4 eV lower than the value for the electrode treated with 1-chloroterdecamethylhexasilane. This difference is only 0.1 eV greater than the sum of the standard deviations. The observation of only one peak for each treated electrode and for dodecamethyloxacycloheptasilane and the similarity of binding energies of silicon on the differently treated electrodes is consistent with π-electron donation from oxygen to polysilicon *groups* instead of just to a vacant orbital on the silicon contiguous with oxygen. A comparable transfer of electron density has been reported for chloropermethylpolysilanes.[1,10]

In conclusion, the following scheme accounts for the products of electrolysis, organosilyl-coated electrodes, the absence of an ESR spectrum, and the observation of a quasi-reversible reduction only with platinum electrons previously conditioned at positive potentials and presumably covered with an oxide layer.
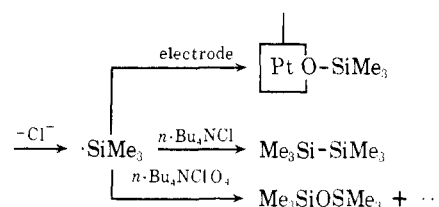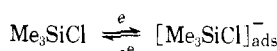
Thus, organosilyl groups can become covalently bound to an electrode surface by an electrochemical process as well as by the chemical reactions reported in ref 3. The possibility of attaching by electroreduction organosilyl groups to other electrodes having oxide surfaces is being investigated.

References and Notes

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