O   denoting the oxidized form
R   denoting the reduced form
i   pertaining to species O and R
c   cathodic
lim   pertaining to the diffusion controlled current

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Analysis of Products from Reactions of Chemisorbed Monolayers at Smooth Platinum Electrodes: Electrochemical Hydrodesulfurization of Thiophenol Derivatives

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The product mixtures from electrochemical hydrodesulfurization of selected thiophenolic compounds chemisorbed through the –SH moiety at smooth Pt electrodes in molar acid have been analyzed quantitatively by using thin-layer electrochemical methods in conjunction with capillary gas chromatography and liquid chromatography. The following compounds were studied: pentafluorothiophenol (PFT), mercaptohydroquinone (MHQ), and 2-mercaptobenzoic acid (MBA). A comparatively high area, large-volume preparative thin-layer electrode (TLE) was constructed to facilitate sample analysis. The results obtained from TLE, GC, and HPLC analysis were in good agreement. The extent of hydrodesulfurization (defined here as simple cleavage of the C–S bond without impairment of the aromatic functionality) depended on the nature of the pendant aromatic ring, decreasing in the order PFT (100%) >> MHQ (50%) >> MBA (15%). Only one desulfurization product was observed for MHQ and MBA; the absence of other products was probably because ring hydrogenation (to form alkyl-type groups) competed with simple desulfurization, and detachment of the alkyl moieties from the –SH anchor occurred with greater difficulty than that of the aromatic group.

Extensive studies on the chemisorption and orientation of a variety of aromatic compounds at smooth polycrystalline Pt electrodes by means of thin-layer electrochemical techniques (*1–4*) have demonstrated that thiophenol derivatives are bound to the surface through the SH moiety (*5*). This mode of attachment is strong as illustrated by the fact (*2*) that the adsorbed thiophenols are not displaced by iodide, a well-known potent reagent for Pt surfaces (*6*). Thin-layer voltammetric and coulometric experiments have also shown that in aqueous electrolyte these chemisorbed thiophenols undergo irreversible electrochemical oxidation and reduction to various degrees depending upon the nature of the group directly linked to the SH moiety (*7–11*). For example, in 1 M perchloric or sulfuric acid, pentafluorothiophenol was found to be completely resistant toward oxidative desorption even at 1.3 V (Ag/AgCl (1 M KCl) reference) but showed a well-defined two-electron cathodic peak at a potential slightly positive of that for hydrogen evolution (*7, 8*); stoichiometric considerations indicated that this peak was due to quantitative hydrodesulfurization (cleavage of the C–S bond without impairment of the aromatic framework) to yield unadsorbed pentafluorobenzene and chemisorbed hydrogen sulfide. Insertion of a –CH$_2$– group between the aromatic ring and the thiol anchor (as in benzyl mercaptan) altered the electrochemical behavior of the adsorbed mercaptan: the chemisorbed species was no longer resistant to oxidation, but the ease of desulfurization also decreased. In the absence of the
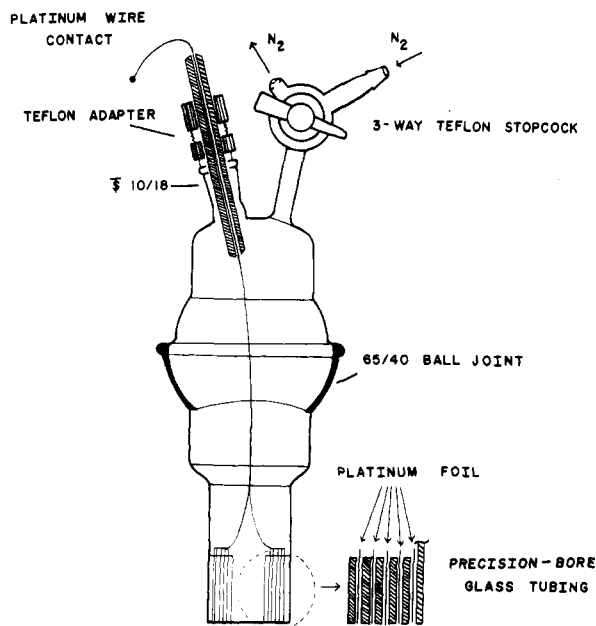
Figure 1. Schematic drawing of the preparative or macro thin-layer electrode.

F substituents, the hydrodesulfurization reaction was further complicated by hydrogenation of the aromatic ring (7, 8).

Although electrochemical experiments led to certain conclusions concerning the outcome of a given surface reaction (7–11), it was necessary to obtain additional information on the product distribution in order to formulate a full description of the surface-reaction pathway. In the present paper, we describe a method for the quantitative analysis of products generated from electrochemical hydrodesulfurization of thiophenol derivatives chemisorbed at smooth polycrystalline Pt electrodes. The analytical methodology involved thin-layer electrochemical (TLE) methods in conjunction with capillary gas and high-performance liquid chromatographic techniques, as described in detail in the next section. Three compounds were studied: pentafluorothiophenol (PFT), mercapto-hydroquinine (MHQ), and 2-mercaptobenzoic acid (MBA); only the latter was studied by both gas and liquid chromatographic analysis.

EXPERIMENTAL SECTION

Preparative Thin-Layer Electrochemical Cell. Thin-layer electrodes (12) are known to be very suitable for surface studies because of (i) the absence of diffusional mass transport between the solution in the bulk and that inside the electrochemical cell, (ii) small cell volume, which minimizes surface contamination; (iii) ease of isolation (for subsequent characterization) of species generated from surface reactions, and (iv) large ratio of surface area to cell volume (A/V), which ensures magnification of surface processes relative to those in solution (1–6). However, the limited surface area (ca. 1 cm^2) and extremely small cell volumes (ca. 4 μL) of conventional thin-layer electrodes would make identification of products generated from surface reactions at smooth (thin-layer) electrodes somewhat difficult. Accordingly, for the present investigation, a comparatively high area, large-volume ("preparative" or "macro") thin-layer electrochemical cell was constructed; a schematic drawing of this cell is shown in Figure 1. The cell consisted of six evenly spaced concentric glass tubes; the outer diameter of the largest tube was 32 mm, that of the smallest tube was 16 mm, and the depth of the cell was 25 mm. The gap or compartment between the concentric tubes was 0.23 mm, and Pt foil 0.13 mm thick was inserted between these compartments. The tubes were fused at the bottom except for four small holes at each compartment to allow for solution entrance and exit. Pt wire was spot-welded at the upper portion of each foil. The macro cell assembly was then attached to a glass holder fitted with a stopcock made of Teflon to enable the use of pressurized inert gas (oxygen-free nitrogen) to expel spent solution from the cell com-

partments; as in conventional thin-layer cells, fresh solution enters into the cell by capillary action. Thin-layer electrodes are available from the Wilmad Glass Co., Buena, NJ.

Prior to the experiments, the Pt foils were thermally annealed to minimize surface roughness (13, 14). Surface pretreatment was done by exposing the clean Pt foil electrodes to dilute (1 mM) aqueous solutions of the subject compounds for at least 180 s. Excess (unadsorbed) reagent was flushed out by thorough rinsing of the macro cell with pure supporting electrode. Electrochemical hydrodesulfurization was carried out potentiostatically at –0.20 V (Ag/AgCl (1 M Cl$^-$) reference) for 60 s. Clean electrode surfaces were regenerated electrochemically by multiple oxidations (at 1.3 V) and reductions (at –0.2 V) in 1 M H$_2$SO$_4$ (1–5); cleanliness was verified by cyclic voltammetric in pure supporting electrolyte (cf. Figure 2). This voltammetric behavior is characteristic of clean polycrystalline Pt, as shown in ref 15 and subsequent studies reviewed in ref 16.

Reagents. Pyrolytically triply distilled water (17) was used as the solvent throughout this study. Mallinckrodt (analytical reagent) sulfuric acid was employed as the supporting electrolyte.

Solvent extractions were carried out with diethyl ether (Burdick and Jackson) freshly distilled from ferrous sulfate heptahydrate (Baker and Adamson). Derivatization reactions were performed in dimethyl sulfoxide (Me$_2$SO, Burdick and Jackson) previously extracted with two portions of diethyl ether to remove unwanted extractable materials and stored over freshly activated type 3A molecular sieves (MCB). Prior to its use in the HPLC experiments, methanol (Aldrich) was passed through a 0.5-μm nylon filter (MSI).

Anhydrous sodium sulfate (Mallinckrodt) and anhydrous calcium chloride (Fisher) were heated to about 450 °C under a stream of nitrogen for 4 to remove extractable organic impurities and then stored in a desiccator over Drierite.

Sodium bicarbonate (Mallinckrodt), sodium chloride (Fisher), tetramethylammonium hydroxide pentahydrate (Sigma), methyl iodide (Mallinckrodt), pentafluorothiophenol (Aldrich, 97%), pentafluorobenzene (Aldrich, 98%), hydroquinone (Aldrich, 99%), methylhydroquinone (Aldrich, 99%), p-benzoquinone (Aldrich, 98%), methyl-1,4-benzoquinone (Aldrich, 98%), 2-mercapto-benzoic acid (Aldrich, 95%), benzoic acid (Aldrich, 99%), m-toluic acid (Aldrich, 99%), methyl benzoate (Aldrich, 99%), and 3-methyl benzoate (Aldrich, 99%) were all used as received. Mercaptohydroquinone (18) and 1,4-naphthohydroquinone (19) were synthesized following published procedures.

Product Analysis. (1) Gas Chromatography. Products obtained from surface electrochemical reactions were analyzed with a Hewlett-Packard 5890A capillary gas chromatograph equipped with a flame ionization detector. Electrolysis products were separated on a 25-m × 0.32-mm-i.d. cross-linked methyl silicone fused silica capillary column with film thickness of 0.52 μm (Hewlett-Packard, Ultra Performance). Samples (1 μL) of concentrated ether extracts were injected into a dedicated on-column capillary inlet system. The identity of all electrolysis products was verified by comparison of gas chromatographic retention times with those of commercially available authentic samples. Gas chromatographic peak areas were integrated with a Hewlett-Packard 3392 integrator. Quantitation of electrolysis products was accomplished through the use of appropriate internal standards; experimentally determined response factors were obtained for each electrolysis product. Product amounts are reported in absolute yields and reflect the percentage of chemisorbed starting material incorporated into a particular species. The surface concentrations of PFT and MHQ were determined empirically by thin-layer coulometry following published procedures (1–5); the surface coverage of the electroinactive MBA in the S-attached orientation was calculated by using space-filling models, which have been shown to yield values in excellent agreement with experiment (1–5).

The actual procedure used in the workup of samples depended upon the nature of the putative products. For water-insoluble products, the following procedure was used: Samples containing electrolysis products in 1 M sulfuric acid were collected by spraying the contents of the macro thin-layer cell cavity into a glass cup cooled with dry ice. After the collected sample was thawed, pooled samples (usually two collections) were extracted with three equal volumes of diethyl ether (ca. 2 mL). The ether extract was treated
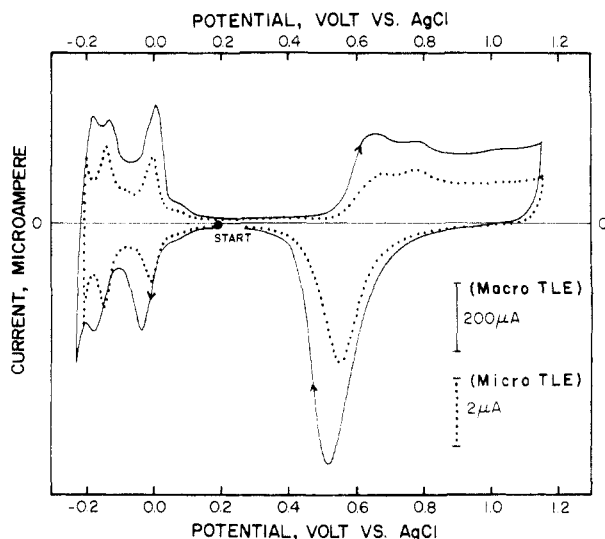
Figure 2. Thin-layer current–potential curves for freshly annealed Pt electrodes in 1 M H_2SO_4: solid curve, macro thin-layer electrode; dashed curve, conventional TLE. The surface area of the macro TLC was 168 cm^2, that of the conventional TLE was 1.16 cm^2. The sweep rate was 1 mV/s.

with 1 mL of 1% sodium bicarbonate and washed with 1 mL of pyrolytically triply distilled water. The ether extract was then dried with anhydrous sodium sulfate for 20 min and concentrated using a gentle stream of nitrogen gas. The volume of ether was reduced to 100 μL prior to gas chromatographic analysis.

For water-soluble products (such as organic acids), the procedure employed was as follows: Pooled samples (usually five collections, ca. 3.5 mL) were extracted with four 5-mL portions of diethyl ether. The combined ether extracts were dried over anhydrous calcium chloride for about 30 min. The volume of ether was then concentrated to about 1 mL (using nitrogen gas purge), and 2 mL of Me$_2$SO was added followed by complete removal of the remaining ether. Esterification of organic acids was done following published procedures (20). Approximately 1 mg of tetramethylammonium hydroxide (pentahydrate) was added to the Me$_2$SO solution followed by 2/μL of methyl iodide. The reaction mixture was stirred overnight at room temperature. The Me$_2$SO solution was combined with 25 mL of ether and extracted with three 5-mL portions of 1 M sodium chloride. The ether extract was then dried with sodium sulfate and later evaporated to an appropriate volume (about 0.5 mL). At least three trials were performed for each analysis.

(2) *High-Performance Liquid Chromatography.* The instrument used for all liquid chromatographic analyses was a Hewlett-Packard 1090 HPLC equipped with a ternary solvent delivery system, a heated sample compartment, a diode array detector, and an HP 79887A multichannel integrator.

Analyses were carried out isocratically on a PRP-1 reverse-phase polymer column (Hamilton Co.) at 40 °C using a 70:30 methanol/water mobile-phase composition. All solutions and analytical samples were filtered through 0.5-μm nylon filters prior to analysis. A flow rate of 0.8 mL/min allowed for analysis times of less than 10 min. Sample injection volumes were typically 10 μL. Column effluents were monitored by UV absorption at 230 nm (bandwidth of 4 nm). The peak areas were found to be linear as a function of volume injected over a fairly wide range.

External standards containing 15 μM benzoic acid and *m*-toluic acid were prepared in 1 M sulfuric acid; the same toluic acid reference solution employed in the HPLC analysis was also used in the macro TLE experiments. HPLC analysis was performed only for MBA, mainly for comparison with the GC results; three trials were also performed for this analysis.

RESULTS AND DISCUSSION

Figure 2 shows current–potential curves for clean, freshly annealed Pt electrodes in 1 M H_2SO_4; the dashed curve was obtained with a conventional TLE (surface area of 1.16 cm^2, cell volume of 3.62 μL), while the solid curve was with the macro TLE. The anodic peak above 0.4 V is due to irreversible
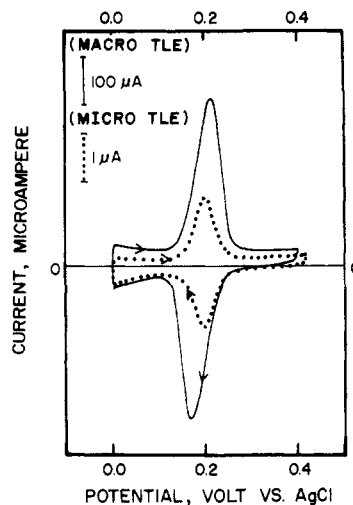

Figure 3. Thin-layer current–potential curves for 0.1 mM 1,4-naphthohydroquinone in 1 M sulfuric acid: solid curve, macro TLE; dashed curve, conventional TLE. The volume of the macro cell was 0.90 mL, that of the conventional cell was 3.62 μL. The sweep rate was 1 mV/s.

formation of surface oxide; its reduction is shown by the sharp cathodic peak centered near 0.5 V (14). The peaks below 0.0 V represent the reversible underpotential deposition of hydrogen atoms onto the polycrystalline Pt surface; the area under these peaks is a direct measure of the number of active sites on the electrode surface (14, 21) As can be seen from the figure, the shapes of the current–potential curves for the conventional and macro TLE's were similar. Quantitative coulometric measurements of the hydrogen-deposition peaks indicated that the electrode surface area of the macro TLE was 168 cm^2.

Current–potential curves for the two-electron naphthoquinone/naphthohydroquinone (NQ/NHQ) interconversion obtained with the conventional (dashed curve) and macro (solid curve) TLE's are shown in Figure 3; the concentration of NHQ was 0.1 mL. It is obvious from this figure that the macro TLE exhibited thin-layer behavior (12) virtually identical to that of the conventional TLE. The area under the redox peak in Figure 3 provides a measure of the thin-layer cell volume; from the present data and from additional experiments using the Fe^{3+}/Fe^{2+} couple, the volume of the macro TLE was found to be 0.90 mL.

Figure 4 gives current–potential curves obtained with the macro TLE in molar sulfuric acid for chemisorbed pentafluorothiophenol (solid curve) and mercaptohydroquinone (dashed curve). (i) A well-defined cathodic peak was observed for PFT at potentials just before evolution of molecular hydrogen. Coulometric measurements based on conventional thin-layer electrodes (8–11) indicated this peak to be due to a two-electron hydrodesulfurization reaction (cleavage of the C–S bond without hydrogenation of the aromatic ring) to produce unadsorbed pentafluorobenzene and chemisorbed H$_2$S as follows:
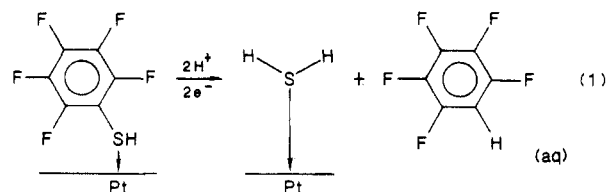
(ii) The desulfurization reaction of MHQ did not occur as readily as that of PFT, as evidenced by the fact that no distinct reductive peak was evident prior to evolution of molecular hydrogen. However, it is clear that hydrodesulfurization took place at −0.2 V, since a subsequent
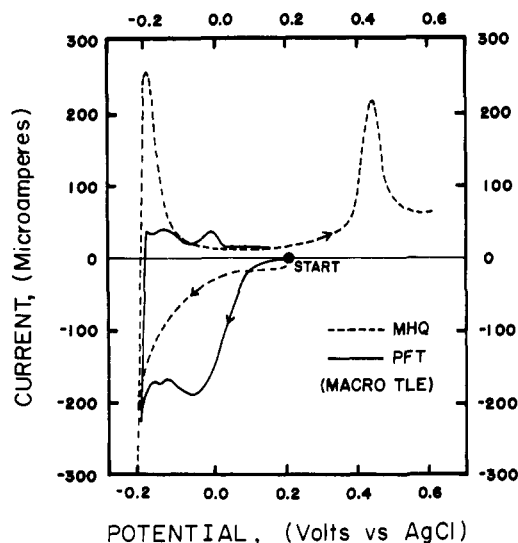
Figure 4. Thin-layer current–potential curves for hydrodesulfurization of pentafluorothiophenol (solid curve) and mercaptohydroquinone (dashed curve) in 1 M H_2SO_4. The macro thin-layer electrode was used to obtain these curves. Experimental conditions were as in Figure 3.
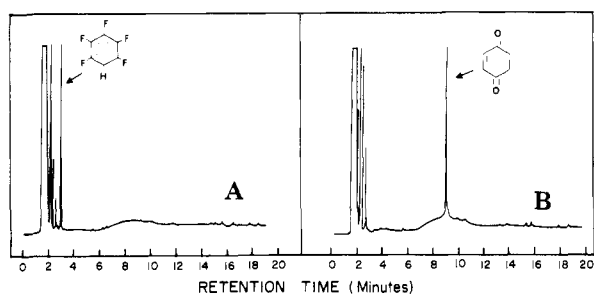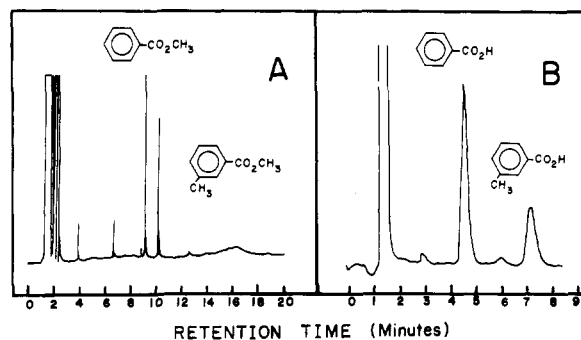

Figure 5. Gas chromatograms of product mixtures obtained after electrochemical hydrodesulfurization of (A) pentafluorothiophenol (PFT) and (B) mercaptohydroquinone (MHQ) chemisorbed at the Pt macro TLE. The hydroquinone product from MHQ was oxidized to benzoquinone at 0.5 V prior to sample workup. The experimental procedures were as described in the text.

positive scan contained a sharp peak at 0.46 V due to *unadsorbed* hydroquinone. Previous experiments using conventional TLE's indicated that the extents of desulfurization and aromatic hydrogenation of MHQ were temperature-dependent (8–11). The current–potential curves for 2-mercaptobenzoic acid were similar to those for MHQ and did not reveal a well-defined hydrodesulfurization peak.

Figure 5 shows gas chromatograms of the product mixtures obtained after 60-s potentiostatic reductions (hydrodesulfurization at −0.20 V) of chemisorbed PFT (Figure 5A) and MHQ (Figure 5B). For the latter experiment, the electrode potential was held at 0.5 V for 60 s immediately after the desulfurization reaction in order to collect the generated product as benzoquinone (BQ) instead of hydroquinone (HQ); sample workup (ether extractions) was more efficient when BQ, rather than HQ, was the product collected. It is interesting to note that for both PFT and MHQ, only one electrogenerated product was detected.

Figure 6A shows the gas chromatogram obtained for the hydrodesulfurization product mixture of MBA; for this particular experiment, 0.015 mM *m*-toluic acid was added as an internal standard prior to sample extraction/workup. The corresponding liquid chromatogram of the MBA desulfurization product mixture is given in Figure 6B. As noted in Figure 6, the prominent peaks observed are due to either benzoic acid (desulfurization product), solvent, supporting electrolyte, or internal standard. Thus, as for PFT and MHQ, only one product from the hydrodesulfurization of adsorbed MBA was observed.

Figure 6. Gas (A) and liquid (B) chromatograms of the product mixture obtained after electrochemical hydrodesulfurization of 2-mercaptobenzoic acid (MBA) chemisorbed at the Pt macro TLE. Peaks other than that of benzoic acid are for the solvent (or supporting electrolyte) and internal standard. The experimental procedures were as described in the text.

Table I. Thiophenol Hydrodesulfurization at Smooth Pt Electrodes

compd	% hydrodesulfurization[a]		
	macro TLE	GC	HPLC
pentafluorothiophenol (PFT)	100 ± 4	100 ± 5	ND[b]
mercaptohydroquinone (MHQ)	53 ± 4	48 ± 5	ND
2-mercaptobenzoic acid (MBA)	ND[c]	16 ± 1	15 ± 1

[a] Hydrodesulfurization is defined here as simple cleavage of the C–S bond without impairment of the aromatic ring. Percentage yield calculations were based on the actual surface coverages of the subject compounds as described in the text. [b] ND, not determined. [c] Benzoic acid, the desulfurization product of MBA, is not electroactive under the conditions presently employed; hence, no TLE electroanalysis was possible. The surface coverage of MBA was calculated (ref 1 and 4) to be 0.57 nmol cm^{-1}.

Table I summarizes the results of quantitative analysis of the product mixture from the electrochemical hydrodesulfurization of the subject compounds chemisorbed at smooth Pt electrodes. (i) The hydrodesulfurization yields obtained from thin-layer electroanalysis of PFT and MHQ were essentially the same as those derived from gas chromatography. This agreement, although not unexpected, is important because it lends confidence to GC analysis for cases (like MBA) in which the desulfurization reaction is ill-defined and the desulfurization products are electrochemically inactive. (ii) The results from GC and HPLC analysis were virtually identical. Analysis by HPLC is desirable because tedious derivatization and/or extraction procedures are not necessary; however, detection by UV–vis spectrophotometry is limited to products (such as the aromatics) that adsorb fairly strongly in that spectral region. (iii) The extent of simple hydrodesulfurization varied with the nature of the aromatic ring attached to the –SH moiety. Under the present conditions, the ease of hydrodesulfurization decreased in the order PFT ≫ MHQ ≫ MBA. This trend is in agreement with heterogeneous catalysis in which fluorine substituents facilitated the desulfurization of thiophenolic compounds (22). Apparently, the presence of two –OH groups enhanced the desulfurization of the aromatic mercaptan to a greater extent than a single –COOH group. (iv) Only one desulfurized product was detected for all three subject compounds, even though the hydrodesulfurization of MHQ and MBA did not go to completion.

Inefficient hydrodesulfurization arises because the aromatic moiety can be hydrogenated while tethered to the –SH group (presumably to form alkyl-type groups). It has been shown that hydrogenation of the aromatic framework at the potentials employed here does not occur unless the aromatic is *attached rather directly* to the surface (7–11). The aro-

matic-hydrogenation side reaction is possible for MBA and MHQ because, as shown in Figure 5B, evolution of molecular hydrogen competes with the hydrodesulfurization reaction; in contrast the desulfurization of PFT was uncomplicated because it took place at potentials where only minute amounts of molecular hydrogen were present. It appears likely that the alkyl group remained on the surface, since, in the chemisorbed state, cleavage of the alkyl C–S bond has been found to occur with greater difficulty than cleavage of the aromatic C–S bond (8–11). If pendant alkyl groups were detached from the sulfur anchor, these would have been readily detected. In addition, voltammetric and coulometric analysis of the surface following hydrodesulfurization indicated that the surface consisted of species more complex than H_2S. That is, if all the organic moieties (aromatic or alkyl) had been cleaved from the sulfur anchor, only H_2S would have remained on the surface and electrochemistry characteristic of chemisorbed hydrogen sulfide would have been observed (7–11), contrary to what was actually found.

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Development of Extended X-ray Absorption Fine Structure Spectroelectrochemistry and Its Application to Structural Studies of Transition-Metal Ions in Aqueous Solution

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Extended X-ray absorption fine structure (EXAFS) measurements were performed on solutions of various transition-metal complexes. Electrochemical methods were used to generate and maintain the materials in a chosen oxidation state. A spectroelectrochemical cell was constructed with a reticulated vitreous carbon electrode and followed the basic design of an optically transparent thin-layer electrochemical cell. Cell performance was tested on ferrocyanide with chronoamperometry, chronoabsorptometry, and cyclic voltammetry. X-ray absorption spectra of cobalt(III/II) sepulchrate were examined in a potentiostatic study. Fluorescence EXAFS spectra of $Ru(NH_3)_6^{3+}$ were evaluated for sensitivity enhancement as a function of concentration. Cytochrome c spectra have been recorded and gave a Fe(III)–N distance of 1.97 Å and a Fe(II)–N distance of 1.99 Å.

Many structural questions of importance in chemistry involve materials that cannot be made crystalline, e.g., amorphous solids and aqueous solutions. The study of these systems was hindered previously by the lack of a technique for determination of local structures. Major advances in the development of synchrotron radiation (1) as a source of X-ray photon flux for absorption spectroscopy and a reinterpretation of the extended X-ray absorption fine structure (EXAFS) phenomenon (2–4) have made structural studies of ions in solution relatively straightforward (5–11). The element specificity of the EXAFS technique allows its application to moderately dilute solutions ($\sim 10^{-2}$ M).

The information contained in EXAFS spectra includes the oxidation state of an absorbing atom, the type and number of atoms surrounding the absorbing atom, and the corresponding bond lengths. Furthermore, absorption features of different elements are well-separated in energy, and thus it is possible to probe the environment of specific elements in a complex sample. Electrochemical methods offer a convenient means for generating complexes in a chosen oxidation state for study through rapid electrolysis.

Basically, in the X-ray absorption experiment an accurate measurement is made of the absorption coefficient, μ, near a particular absorption edge as a function of the photon energy