Mechanism of Spontaneous Formation of Monolayers on Gold from Alkyl Thiosulfates

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ABSTRACT: The kinetics of adsorption of self-assembled monolayers (SAMs) from solutions of hexadecyl thiosulfate in tetrahydrofuran was studied under a variety of experimental conditions to elucidate the mechanism(s) important in this process. Monolayers did not form in the absence of water, which ruled out the direct addition of the alkyl thiosulfate to the gold surface and implicated hydrolysis as a route to surface-active adsorbates. The role of tetrafluoroborate ion, known to inhibit SAM formation in this system, was also examined. These studies, too, were consistent with hydrolysis as an intermediate step in the formation of monolayer films in this system.

INTRODUCTION

Chemisorption of organic thiols or disulfides on gold provides a fast, convenient method for the formation of well-ordered monolayers on gold substrates.1,2 One challenge with using these self-assembled monolayers (SAMs) to articulate surface structure is forming them selectivity on substrates bearing more than one gold feature. To address this problem, we have reported an electrochemical method for the selective formation of SAMs from alkyl thiosulfates (Bunte salts).3–5 Using this method, a SAM can be formed on a particular microelectrode and not on neighboring ones. Curiously, SAMs can also form spontaneously from solutions of alkyl thiosulfates on gold and copper surfaces, as well as gold and silver nanoparticles, in the absence of an applied potential.6–12 In control experiments, we showed that the presence of tetrafluoroborate ion in the electrochemical system inhibited this spontaneous adsorption and allowed the observed selective formation of SAMs. In the absence of the tetrafluoroborate ion, SAMs indeed formed spontaneously from solutions of Bunte salts in tetrahydrofuran and complete formation required 10–15 min at room temperature.

This inhibition of the spontaneous adsorption of SAMs is critical to the regioselectivity allowed by electrochemically assisted chemisorptions, so we have studied the mechanism of the spontaneous process, in hopes of gaining a greater understanding of how it occurs and how it is inhibited by tetrafluoroborate ion. At the outset of our studies, we recognized two possible types of mechanism that could lead to spontaneous chemisorption of SAMs on gold from solutions of alkyl thiosulfates (Scheme 1). One possibility is direct reaction between the alkyl thiosulfate and the gold surface, leading to cleavage of the sulfur–sulfur bond to produce chemisorbed alkyl thiolate and weakly bound sulfite ion.6–12 A second possibility is initial reaction of the alkyl thiosulfate in solution to form a species such as alkanethiol or disulfide that could subsequently chemisorb at the gold surface. Either the direct or indirect process might be inhibited by tetrafluoroborate ion.

EXPERIMENTAL SECTION

General. Hexadecanethiol (Aldrich, 92%) was purified by distillation under vacuum prior to use. Tetraetylammmonium tetrafluoroborate (TCI America, 98%), and 1-bromo-n-hexadecane (Sigma-Aldrich, 97%) were used as received. Sodium thiosulfate pentahydrate (Fischer Scientific, >99%) and absolute ethanol (EtOH; Pharmco Solvents) were used as received. Tetrahydrofuran (THF) was obtained either from ACROS Organics (99.9%) and distilled from sodium-benzophenone ketyl, or from EMD Chemicals (Omnisolv) and purified and dried using a PureSolv system before use. Concentrated sulfuric acid (EMI Scientific, 95.0–98.0%), hydrogen peroxide (VWR, 30%), and isopropanol (VWR, IPA; 99%) were used as received. 3-Mercaptopropyltrimethoxysilane (MPS) was purchased from Gelest and used as received. Hexadecane (Fischer Scientific, 99%) used in contact angle measurements was purified by percolation twice through activated alumina. Glass microscope slides (25 × 75 mm) were purchased from VWR. The water used in this work was purified with a Millipore Milli-Q system to a purity of 18 MΩ cm using a Milli-Q purification system.
resistivity of at least 15 MΩcm. 1H NMR spectra were acquired using a Bruker AMX 500 spectrometer, referenced to residual methyl protons in CD<sub>3</sub>OD at 3.30 ppm or to the residual protons in CDCl<sub>3</sub> at 7.24 ppm, and are reported in units of δ. Borosilicate scintillation vials were purchased from Fischer Scientific, and the polyethylene cap was replaced with aluminum foil to avoid contamination.

**Sodium Hexadecylthiosulfate, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>S<sub>2</sub>O<sub>3</sub>Na.** This Bunte salt was prepared following literature procedures. The 1-bromo-hexadecane (1.527 g, 5.001 mmol) was dissolved in 20.0 mL of absolute ethanol and then added to a solution containing sodium thiosulfate pentahydrate (1.241 g, 5.000 mmol) in 20.0 mL of water. The mixture was refluxed until it became homogeneous (18–20 h). The solution was then cooled to room temperature, allowing the hexadecylthiosulfate to precipitate. The white solid was filtered and rinsed with water until the filtrate collected was clear. The white solid was then recrystallized from hot ethanol. As reported elsewhere, this compound crystallizes with approximately a third of an equivalent of water, which can be removed slowly under vacuum. Unless otherwise noted, the hydrated solid was used in the studies reported here. 1H NMR in CD<sub>3</sub>OD: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>S<sub>2</sub>O<sub>3</sub>Na, 0.90 ppm (t, 3H); CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>S<sub>2</sub>O<sub>3</sub>Na, 1.30–1.40 ppm (m, 26); CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>2</sub>S<sub>2</sub>O<sub>3</sub>Na, 1.74 ppm (q, 2H); CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>2</sub>S<sub>2</sub>O<sub>3</sub>Na, 3.05 ppm (t, 2H).

**Preparation of Gold Substrates.** Microscope slides were cut into 1.0 cm × 2.5 cm pieces, and each was wiped with Kimwipes to remove any visible lint on the surface. Gold substrates were then prepared in one of two ways. Method 1: The slides were cleaned by immersion in 1:4 (v/v) H<sub>2</sub>O<sub>2</sub>/concentrated H<sub>2</sub>SO<sub>4</sub> (piranha solution) at 70.0°C for about 20 min. Caution! Piranha solution reacts violently with organic materials and should be handled with extreme care. The slides were rinsed with water, dried with a stream of nitrogen, and then heated in an oven at 105 °C for about 10 min. After cooling to room temperature, the slides were treated with MPS to enhance adhesion to gold. Clean slides were added to a refluxing solution of MPS (7.524 g, 38.32 mmol) and water (7.478 g, 415.1 mmol) in 283.0 mL of IPA for 10 min. The slides were then rinsed with THF, EtOH, and water, followed by a thorough drying under a stream of nitrogen. Contact angles of hexadecane were measured, and the sample was rinsed using the same sequence as above. Before re-entering the glovebox, the slides were stored in a vacuum-sealed desiccator until use. Gold (99.999%) films with a thickness of ∼1000 Å were deposited by e-beam evaporation at a rate of ∼8 Å/s. Method 2: Microscope slides were cleaned with piranha solution, rinsed extensively with water, dried with a stream of nitrogen, and then stored under vacuum until use (usually within 1 day). A thin (∼50 Å) layer of titanium (99.99%) was deposited on the slides as an adhesion promoter, followed by ∼2400 Å of gold (99.999%) at a rate of 4 Å/s, via e-beam evaporation.

**Recycling of Gold Substrates.** Gold substrates bearing SAMs were recycled using a modified literature method, in a UVCOS ultraviolet cleaning system. The substrates were exposed to an oxygen/ozone atmosphere for 5 min under a low-pressure quartz mercury-vapor lamp with UV emission in the range of 185–254 nm. Immediately following the oxidation, the gold-coated samples were immersed in pure ethanol for 20 min without stirring, to reduce any gold oxide(s).

The times necessary for effective oxidation and reduction were determined using the following control experiments. To test the oxidation time, surfaces bearing SAMs were treated with UV-ozone for 5, 10, 20, or 30 min and then were soaked for 20 min in EtOH at room temperature without stirring. After this treatment, each of the gold samples was wet by hexadecane (advancing contact angles < 10°), consistent with the literature. The substrates were then rinsed with THF, EtOH, and water, and SAMs were formed electrochemically from n-hexadecylthiosulfate. The advancing contact angle of hexadecane was 44–46° on all of the samples, consistent with complete SAMs. We used 5 min treatments in our studies, as they gave results indistinguishable from those following longer treatments.

A similar set of experiments was performed to find the optimal time necessary for reduction by EtOH. Samples of SAMs on gold were initially treated for 5 min with UV-ozone, followed by treatment with EtOH for 10, 20, 30, or 40 min without stirring. Again, the effectiveness of the treatment was assessed by formation of a SAM from sodium n-hexadecylthiosulfate electrochemically and measurement of contact angles of hexadecane. Samples that had been treated with EtOH for 10 min had advancing contact angles of hexadecane of ∼30°, indicating an incomplete monolayer. Treatment for 20, 30, and 40 min, in contrast, allowed formation of complete SAMs with advancing contact angles of hexadecane in the range of 44–46°. As a result, 20-min treatments with EtOH were used in our experiments.

**Contact-Angle Measurements.** Advancing contact angles of hexadecane and water were measured with a Rame-Hart NRL model 100 goniometer. A minimum of six measurements on three independent drops were made for each sample.

**Inert-Atmosphere Study.** Dry tetrahydrofuran was collected using a glass syringe and transferred to an Ar-purged Schlenk flask, which was then sealed and transferred into a nitrogen-filled glovebox. A 25.00-mL volumetric flask — covered with a perforated Kimwipe secured with a rubber band to prevent the loss of any flakes of sodium n-hexadecylthiosulfate (9.0 mg, 25 μmol) — and a gold sample were dried overnight in the antechamber under dynamic vacuum prior to entry into the glovebox. Control experiments suggest that this vacuum treatment would have removed most or all of the water that typically crystallizes with this alkyl thiosulfate. A solution of the alkyl thiosulfate (1.0 mM in THF) was formed inside the glovebox, and the gold sample introduced.

To make contact-angle measurements, the Au sample was removed from the solution inside the glovebox and rinsed once with dry THF. It was placed into a scintillation vial, which was then sealed and removed from the box. Outside the glovebox, the slide was rinsed with THF, EtOH, and water, followed by a thorough drying under a stream of nitrogen. Contact angles of hexadecane were measured, and the sample was rinsed using the same sequence as above. Before re-entering the glovebox, the sample was allowed to dry in the evacuation chamber under dynamic vacuum for ∼20 min. It was then placed back into the solution.

**Kinetic Dependence on Ambient Water Vapor.** A small glovebag was purged with and maintained under a positive pressure of dry house air. The relative humidity inside the bag was measured with a dial hygrometer and remained in the range of 2–4%, and the ambient relative humidity of the room was ≥25%. Dry tetrahydrofuran was collected in an Ar-purged flask that was then sealed until it was introduced into the glovebag. Sodium n-hexadecylthiosulfate was dried under dynamic vacuum for at least 24 h before use to remove any water of hydration. In the glovebag, 25 mL of a solution containing 1 mM sodium hexadecylthiosulfate and 0.1 mM tetrabutylammonium tetrafluoroborate was formed using the dry THF. Half of this solution was poured into a vial containing a gold sample and kept in the bag. The other half was poured into a second vial with a gold sample, removed from the bag, and exposed to the ambient atmosphere of the room. The vials were not capped, and both solutions were stirred magnetically throughout the experiment. After 5 min intervals, each gold sample was removed from its vial and rinsed with THF, ethanol, and water. Contact angles of hexadecane were measured, and the samples were then rinsed as before and returned to their respective vials. Kinetics data for adsorption from a solution containing a high concentration of dissolved oxygen are provided in the Supporting Information.

**Kinetic Dependence on [Bu<sub>4</sub>NBF<sub>4</sub>]**. A stock solution of sodium n-hexadecylthiosulfate (1.0 mM in THF) was prepared in a volumetric flask. From the stock solution, 15 mL aliquots were pipetted into separate vials containing different masses of Bu<sub>4</sub>NBF<sub>4</sub>. A separate piece of gold was placed into each vial. After various intervals, the Au slides...
were removed, rinsed with THF, EtOH, water, and dried under nitrogen before measurements of contact angle.

# RESULTS AND DISCUSSION

**General Characteristics of Spontaneous Monolayer Formation.** Scheme 1 presents two possible routes to the formation of self-assembled monolayers from solutions of alkyl thiosulfates. One possible mechanism that could lead to spontaneous adsorption of SAMs on gold from alkyl thiosulfates would involve direct reaction (e.g., oxidative addition) between the surfactant and the gold surface, followed by loss of a sulfite species from the surface. A second possibility is reaction of the alkyl thiosulfate in solution, followed by adsorption of a surface-active product of that reaction. Alkyl thiosulfates are thermally stable at room temperature, but they do hydrolyze to form thiols or disulfides, and these reactions are catalyzed by acid and by base, respectively. Both thiols and disulfides, of course, readily absorb on gold to form SAMs spontaneously.

To distinguish between direct Au-mediated and indirect hydrolysis mechanisms for spontaneous SAM formation, we treated a gold sample with a THF solution of sodium n-hexadecylthiosulfate in an inert-atmosphere glovebox. The solution was formed and gold sample treated under nitrogen, and the sample was only removed to monitor monolayer formation by measuring the contact angle of hexadecane on the surface. Not only were oxygen and water excluded from the atmosphere above the gold sample and solution, but the application of vacuum (antechamber) that preceded entry into the glovebox very likely also removed any water of hydration associated with the ionic headgroup in the solid alkyl thiosulfate. No tetrafluoroborate ion was added to the solutions, so that the observed kinetics would reflect only the inherent reactivity or inertness between the alkyl thiosulfate and gold.

In this experiment, a SAM did not form, even after weeks of soaking at room temperature (Figure 1). After 1 month, the contact angle of hexadecane had only risen to the mid-20°, rather than the mid-40°'s characteristic of a complete SAM. For comparison, another gold sample was treated analogously in air, and in this case monolayer formation was fast, with the contact angle of hexadecane rising to ~46° within 15 min (Figure 1). Thus, the inhibition of SAM formation provided by the absence of air was much greater than that provided by the presence of 0.100 M tetrafluoroborate. These results ruled out any direct Au-mediated mechanism that does not involve another reactant or catalyst found in air. Given the known hydrolysis chemistry of Bunte salts to produce surface-active precursors to SAMs, these results indicated that water is likely necessary for spontaneous adsorption to occur via prior hydrolysis in solution. This suggestion is also consistent with the reported spontaneous adsorption from solutions that had been deaerated but not dried.

Nonetheless, it is possible that the absence of other components of air (e.g., O₂, O₃) in the glovebox might also be important. We therefore conducted an additional experiment, in which the water content of the atmosphere was the only variable and other components were constant. We compared the kinetics of SAM formation from solutions exposed to dry air (2–4% relative humidity) in a glovebag and to air at ambient humidity (≥25% relative humidity). Thus, both solutions could adsorb oxygen or other species from the atmosphere, but they should contain different amounts of dissolved water.

In our initial experiments, no Bu₄NBF₄ was added to the solutions (1 mM CH₃(CH₂)₁₅S₂O₃Na) in order to mirror the conditions used in the inert-atmosphere study. In these trials, however, the formation of SAMs was rapid, and a complete monolayer had formed under both the dry and humid atmospheres prior to the first measurement. Only a small extent of hydrolysis would be necessary to produce enough thiol to form a SAM, and the results indicated that enough water was present in even the nominally “dry” solutions to produce a SAM quickly. In order to slow the hydrolysis so that any kinetic differences could be measured, we took advantage of the inhibitory effect of tetrafluoroborate ion in subsequent experiments.

Kinetics runs were carried out using solutions containing 1 mM CH₃(CH₂)₁₅S₂O₃Na and 0.1 mM Bu₄NBF₄. This concentration of tetrafluoroborate ion is 10³ times smaller than that used in the electrochemical experiments in which it serves as a supporting electrolyte. In all of these experiments, the monolayer growth, as judged by the advancing contact angle of hexadecane, was significantly faster in the more humid (ambient) environment. In fact, in two of three runs, the SAM was complete (θₐ = 45°) in the more humid environment with 5 min, while the sample in the dry air of the glovebag showed no change in wettability (i.e., wet by hexadecane). Aside from relative humidity, the composition of the two atmospheres was approximately equal. We therefore conclude that the exclusion of water in the original glovebox experiment was responsible for the slower adsorption of the sample in it. These results are consistent with the hypothesis that hydrolysis of the Bunte salt is required for SAM formation in this system.

To confirm these conclusions, we also examined the influence of excess oxygen on the kinetics of spontaneous monolayer formation. We reasoned that if oxygen were a necessary reagent for adsorption, increasing its concentration might increase the rate of this process. In this experiment, the kinetics of SAM formation was monitored for a gold surface in a THF solution containing 1.0 mM sodium n-hexadecylthiosulfate and 0.100 M Bu₄NBF₄ and saturated with oxygen. The experiment was conducted in air. The solution was sparged with O₂ for 5 min prior to immersion of the gold sample, and then again for 5 min each time the sample was removed to measure its contact angle.
Solvant was added during the course of the experiment to maintain an approximately constant concentration of the alkyl thiosulfate and electrolyte. In this experiment, spontaneous formation of a SAM required several days to reach completion, as judged by the contact angle of hexadecane on the surface. Because adsorption of a complete SAM also required several days in analogous solutions that had not been saturated with oxygen, we conclude that the presence or absence of water, and not O\textsubscript{2}, is the most important adventitious reagent in the spontaneous adsorption process.

Specific Features of the Spontaneous Formation of SAMs on Gold from Alkyl Thiosulfates. A nearly ubiquitous feature of the kinetics of spontaneous formation of SAMs in these studies was an immediate rise in contact angle, followed by a slower growth phase (Figure 2). To explain the two-phase kinetics, we hypothesized that the initial rise in contact angle might be due to a small amount of thiol or disulfide contaminants in our solutions of alkyl thiosulfates. The slower phase, we inferred, may then be due to rate-determining hydrolysis of the alkyl thiosulfate to form a higher concentration of the surface-active thiol or disulfide. Although samples of CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{15}S\textsubscript{2}O\textsubscript{3}Na are typically clean by \textsuperscript{1}H NMR, this compound does hydrolyze slowly in the solid state to give the corresponding thiol and disulfide. For example, spectra of a sample stored for months contained small resonances characteristic of both CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{15}SH and [CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{15}S\textsubscript{2}]\textsuperscript{2}. Comparison of the relative integrations of the resonances due to the methylene group adjacent to sulfur in the alkyl thiosulfate, thiol, and disulfide allowed quantification of the thiol/disulfide contamination as approximately 3–4% each.\textsuperscript{20}

To confirm that the contamination by thiol/disulfide was responsible for the initial rise in contact angle, a sample of solid sodium n-hexadecylthiosulfate was rinsed with methylene chloride to remove any corresponding thiol or disulfide. After drying under aspirator vacuum, the sample was dissolved in THF with Bu\textsubscript{4}NBF\textsubscript{4}. A gold film was immersed in the solution (1.0 mM CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{15}S\textsubscript{2}O\textsubscript{3}Na; 0.100 M Bu\textsubscript{4}NBF\textsubscript{4}) and its contact angle of hexadecane measured periodically to monitor any monolayer growth. The results of this study are shown in Figure 3. As expected, an initial and abrupt rise in contact angle was absent for this sample.

After having examined the initial rise in contact angle, we then focused on the apparent induction period at the onset of the slower phase of the kinetics (see Figure 2), a period during which there is only a gradual increase in the contact angle of hexadecane over several days. At some point, the increase in contact angle accelerates, indicating an increasing rate of monolayer formation. These features of the kinetics are understandable if hydrolysis of alkyl thiosulfate to thiol is a central component of this process. The hydrolysis reaction is catalyzed by acid and produces bisulfate as a byproduct (eq 1); thus, it may be self-catalyzed, a feature that would explain the rate acceleration after the induction period apparent at intermediate times in Figure 2.

\[
\text{CH}_3(\text{CH}_2)_{15}\text{S}_2\text{O}_3\text{Na} + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{CH}_2)_{15}\text{SH} + \text{NaHSO}_4
\] (1)

To test this possibility, solutions of alkyl thiosulfate and tetrafluoroborate ion were aged prior to their exposure to gold. If a solution-phase process were responsible for the production of one or more surface-active organosulfur species, aging should give the system time for those species to form and should be reflected in a shorter induction time before the accelerated formation of a SAM. In these experiments, a stock solution of sodium n-hexadecylthiosulfate (1.0 mM) and Bu\textsubscript{4}NBF\textsubscript{4} (0.100 M) in THF was prepared, and 15 mL aliquots were removed for adsorption studies. One aliquot was used immediately to treat a sample of gold. A second aliquot was taken after the solution had aged for 4 days, and then a gold sample was added to it. As shown in Figure 4, the solution used immediately after its preparation caused a small initial rise in contact angle of hexadecane, followed by a pronounced induction period lasting approximately 4 days. The contact angle then began to increase again, but required another 4 days or so to reach a value characteristic of a complete SAM (46°). In contrast, the solution allowed to age for 4 days without gold present produced a monolayer immediately instead of requiring the additional 4 days. Hence, gold appears to slow monolayer formation, not facilitate it, if present during the induction period.

This result indicates that the solution-phase reactivity that produces enough surface-active organosulfur species to form a
complete SAM likely involves more than just hydrolysis, as we would not expect gold to inhibit the hydrolysis reaction. A possible reaction that could explain these results is nucleophilic displacement of bisulfite from alkyl thiosulfate by thiol (eq 2), a known method for the synthesis of dialkyl disulfides in weakly acidic solution. 21

\[
\text{H}_3\text{C}[(\text{CH}_2)_{15}\text{S}_2\text{O}_3\text{Na} + \text{CH}_3(\text{CH}_2)_{15}\text{SH} \rightarrow [\text{CH}_3(\text{CH}_2)_{15}\text{S}]_2 + \text{NaHSO}_3 \quad (2)
\]

A gold surface could, in principle, inhibit such a process by scavenging the thiol present initially in solution or that produced from hydrolysis of the alkyl thiosulfate.

**The Inhibitory Role of Tetrafluoroborate Ion.** Previously, we showed that inhibition of the spontaneous adsorption of SAMs from solutions of alkyl thiosulfates in THF was related to the amount of tetrafluoroborate ion present in solution. Here, we report the kinetics of adsorption from solutions containing various concentrations of Bu$_4$NBF$_4$. In the absence of Bu$_4$NBF$_4$, monolayer formation proceeded to near completion within 15 min from a 1.0 mM solution of sodium n-hexadecylthiosulfate in THF, consistent with our previous experiments. As expected, higher concentrations of tetrafluoroborate ion slowed the kinetics of adsorption of a complete SAM. All of the plots in Figure 5 showed an immediate rise in contact angle (to $\sim 30^\circ$) due to small amounts of thiol or disulfide impurities (vide supra), followed by the familiar slower phase of the kinetics which led to a full monolayer over the course of several days.

To examine whether this inhibition occurs by slowing the hydrolysis reaction or by interfering with adsorption of the thiol produced by it, we compared the kinetics of monolayer growth from solutions that had been aged for 1 day with and without added tetrafluoroborate ion. If the hydrolysis is inhibited by BF$_4^-$, the solutions should behave very differently, with the tetrafluoroborate-free solution producing a much higher concentration of surface active thiol than the tetrafluoroborate-containing solution. Alternatively, if BF$_4^-$ interferes with the adsorption of thiol, but not the hydrolysis reaction that produces it, the two solutions should behave similarly.

Two solutions of sodium n-hexadecylthiosulfate (1.0 mM) in THF were prepared, one with and one without added Bu$_4$NBF$_4$ (0.100 M) and aged for 1 day. A gold substrate was placed into each solution, and contact angles of hexadecane were monitored as a function of time (Figure 6). After 20 min, SAM formation was complete from the solution that did not contain BF$_4^-$, but was far from complete from the one that did (dashed line, Figure 6). A third solution of sodium n-hexadecylthiosulfate (1.0 mM) in THF was aged for 1 day, and then Bu$_4$NBF$_4$ was added (0.100 M). A complete SAM formed within 5–10 min, indicating that BF$_4^-$ does not inhibit SAM formation once thiol had already formed.

These results demonstrate that the inhibitory effect of tetrafluoroborate ion is at least coincident with the hydrolysis of the Bunte salt because adding this ion after hydrolysis has occurred...
had little or no effect. We infer, therefore, that tetrafluoroborate ion likely slows the rate of hydrolysis of alkyl thiosulfates, rather than interfering with chemisorption of the products of hydrolysis. A possible explanation for the role of tetrafluoroborate in inhibiting hydrolysis in this system is the ability of this ion to form complexes with hydronium ion in organic solvents. Such complexion could make the water less available for hydrolysis of the alkyl thiosulfate and therefore slow the kinetics of the process.

**CONCLUSIONS**

The spontaneous formation of self-assembled monolayers on gold from THF solutions of alkyl thiosulfates does not occur via direct reaction between the gold surface and the adsorbate precursor. Instead, kinetic studies under a variety of experimental conditions suggest that SAM formation proceeds via initial hydrolysis of the precursor in solution, followed by adsorption of the product alkanethiol along the well-documented pathway. The inhibitory role of tetrafluoroborate ion in these systems appears to relate to its ability to slow the hydrolysis reaction, perhaps by sequestration of water. These results reveal the importance of considering generally (i) whether the behavior of solutions of alkyl thiosulfates, particularly in self-assembly, involves these compounds as direct reactants or simply as precursors to other organosulfur species (e.g., thiols) that are known to have activity, and (ii) whether any differences between the behavior of these solutions and those of alkanethiols are due to different inherent reactivity of the two solutes or just to differences in the concentration of alkanethiol.

**ASSOCIATED CONTENT**

Supporting Information. Advancing contact angles of hexadecane on a gold electrode as a function of time in contact with an oxygenated solution of n-hexadecylthiosulfate; NMR spectrum of an aged sample of n-hexadecylthiosulfate in deuterated methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**

(20) A representative $^1$H NMR spectrum of an aged sample containing a small amount of thiol contamination is provided in the Supporting Information.