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Sulfonation of Alkyl Phenyl Ether Self-Assembled Monolayers

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Received June 11, 2009. Revised Manuscript Received November 27, 2009

The sulfonation of phenyl ether decorated self-assembled monolayers (SAMs) was studied with an eye toward creating surfaces with a particularly high negative charge density based on a close-packed array of phenyl rings with more than one sulfonic acid group per molecule. The product distribution and kinetics of this process were studied by ultraviolet, infrared, and photoelectron spectroscopies and by monitoring changes in the thickness and wetting properties of the SAM. The sulfonation chemistry could be effected without undermining monolayer integrity and the isomer distribution of ortho- and para-monosulfonated material, along with the percentages of mono- and disulfonated molecules could be established throughout the process. As doubly sulfonated molecules appeared, the reaction slowed drastically. Ultimately, sulfonation stops completely with approximately 60% of the molecules disulfonated and 20% each of the two monosulfonated isomers. This striking constraint on monolayer reactivity and the relationship between the surface chemistry and variations in SAM structure are discussed.

Introduction

Self-assembled monolayers (SAMs) enable the fabrication of molecularly tailored interfaces with precisely controlled physical and chemical properties.^{1–3} The most commonly studied SAMs are based on siloxanes^{4,5} and phosphonates^{6,7} linked to oxide surfaces or thiols attached to the surface of coinage metals.^{1,8,9} The alkyl thiols are well suited for the direct preparation of functionalized monolayers.^{1,3,10} The phosphonates offer a similar advantage.⁷ However, the siloxane-anchored SAMs (despite being more robust) are limited in terms of the range of functional groups that can be installed by direct SAM deposition due to the reactivity of the halo- and alkoxysilanes from which they are made.^{5,11} Thus, the chemical diversity of siloxane-anchored

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SAMs is often achieved using in situ functional group transformations analogous to those typical of bulk media.^{5,12–26}

Reactions that occur at interfaces often differ from their solution analogues.^{27–38} The rates and products of interfacial reactions, for example, often show significant dependence on surface structure. The number of examples 32-38 that clearly address these issues is limited, in large part, because of the difficulty in devising appropriate model systems and in applying the standard approaches of physical organic chemistry to interfacial reactions.

Much remains to be learned about how the incorporation of reactive groups in monolayers influences their reactivity. It is known that the anisotropy and packing of a monolayer can have a strong influence.^{13,32,37,39,40} These differences are often referred to

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as "confinement effects".^{28,39} Key factors in controlling the choice of reaction pathway can also be the proximity of adjacent molecules in the SAMs (kinetic control) as well as shifts in an equilibrium (thermodynamic control).⁴¹ In some cases, this leads to an increase in reactivity^{42–44} and in others there is no detectable effect.^{45,46} In most cases, such reactions are significantly slower than in solution.^{13,33,45,47,48} This reduction in reaction rate can also be accompanied by a nonlinearity such that the reaction rate gets progressively slower as the reaction progresses. An example of this is the exchange of SAM-bound thiols with molecules from solution. Such reactions in well-ordered SAMs have been reported to show rapid exchange at grain boundaries, defects, and other disordered regions while the same process in the crystalline domains takes much longer to reach a steady state and is often only partially complete (30-60%).^{20,49–51}

Mrksich and co-workers studied the Diels–Alder reaction of a soluble cyclopentadiene and a surface-immobilized quinone and showed that it displayed an unusual kinetic profile.²⁷ The reaction follows first-order kinetics when methyl-terminated SAM-forming molecules provide the surrounding microenvironment versus the more expected bimolecular, second-order Diels–Alder reaction when it is done within hydroxyl-terminated SAMs.^{27,52}

There are also examples where monolayer-based constraints alter the balance among reaction products. Such an observation has been made by Chi and Choi⁴¹ when they treated SAMs of 16-mercaptohexadecanoic acid on gold with cyanuric fluoride and pyridine. This generally makes acid fluorides from carboxylic acids, but, in the monolayer setting, mixtures of acid fluorides and interchain carboxylic anhydrides were directly obtained by reaction between neighboring molecules.

The analysis of reaction products produced within an anchored monolayer is often difficult. This limitation is particularly pronounced for reactions that produce a mixture of isomers. Among the limited examples of such studies are the study of a Diels–Alder reaction using cyclic voltametry²⁷ and the regio- and stereoselective complexation described by Maeda et al.⁵³ which separately identified the four different conjugates of *o*- or *p*-methyl red and (*R*)-(+)- or (*S*)-(-)-1-phenylethylamine.

Recently, we have described the sulfonation of benzene rings anchored by a polymethylene chain to the surface of a well-packed SAM.⁵⁴ This reaction converted hydrophobic aryl terminated surfaces into hydrophilic surfaces that possesed substantial negative charge. We developed a detailed analysis for the mixture of *ortho* and *para* sulfonates formed. While the product distributions changed as a function of reaction conditions, they showed, in general, a significant preference for *p*-sulfonate formation along with a subtle but progressive slowing of the reaction and a possible odd—even effect based

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Scheme 1. Sulfonation of Alkyl Benzene SAMs To Form *p*- and *o*-Sulfonates^{54,55}



on the length of the tethering alkyl chain.^{54,55} The product distributions obtained in these studies are broadly summarized in Scheme 1.

SAMs (designated **SAM1** and **SAM2**) based on phenyl ethers **1** ((10-phenoxydecyl)trichlorosilane) and **2** ((11-phenoxyundecyl)trichlorosilane) are expected to be particularly reactive toward electrophilic aromatic substitution due to the higher electron density of their aromatic rings. Compounds **1** and **2** resemble the previously studied alkylbenzenes⁵⁴ except for the replacement of a methylene group with an ether oxygen. Literature precedent suggested that phenyl ethers readily undergo disulfonation.^{56,57} Moreover, the tilt angle of the phenyl ring (relative to the surface) in alkyl phenyl ether monolayers should be different than that of the alkylbenzene system,⁵⁸ and this might influence the reactions of the surface bound molecules.

Having previously reported detailed structural information about close packed siloxane-anchored SAMs of phenyl ethers,⁵⁹ we report herein the sulfonation of such substrates (Scheme 2). Possible steric and charge density constraints raise the question of the extent of double sulfonation that might be achieved in such close-packed monolayer surfaces.

Determining the composition of the sulfonated SAM required the preparation and characterization of suitable spectroscopic model compounds.^{54,55} The sulfonated anisole derivatives prepared in this work are shown in Scheme 3.

We report herein that the different length tethers⁶⁰ of SAM1 and SAM2 do in fact lead to differences in the initial isomer distribution of the monosulfonation reaction. More importantly, the continued sulfonation of the SAM-tethered phenyl ethers stops after ~60% conversion to disulfonate, leaving roughly equal amounts of the ortho and para monosulfonated isomers. This striking retardation of the second sulfonation and the constraints of the monolayer environment that prevent the creation of a more densely sulfonated interfacial layer are the focus of this paper. The kinetics and product distributions for SAM1 and SAM2 over the entire course of the reaction and the attempted sulfonation of an authentic monosulfonated SAM (made by depositing trichlorosilane 4 and oxidizing it in situ; Scheme 4) all provide new insight into the effects of packing, polarity and charge density on reactions at the monolayer surface.

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Scheme 3. Sulfonated Anisole Model Compounds



Scheme 4. Deposition and Oxidation of S-4-(11-undecyloxy)phenylethanethioate Trichlorosilane (4) to Produce an Authentic Para Mono-Sulfonated SAM4ox



Experimental Section

The syntheses and purifications of compounds 1, 2, 3a, 3b, 3c, 3d, and 4 and their detailed characterizations are described in the Supporting Information.

Model Reactions of Electrophilic Aromatic Sulfonation -General Procedure. Four different sets of solution sulfonation conditions were used: (a) concentrated H_2SO_4 at 5 °C; (b) concentrated H_2SO_4 at 25 °C; (c) concentrated H_2SO_4 at 85 °C; (d) concentrated H_2SO_4 + trifluoroacetic anhydride (TFAA) at 10 °C. The sulfonating agent (~10-fold excess for a-c and ~5fold excess for d) was placed in a vial and anisole was added while the vial was held at the indicated temperature. Aliquots were withdrawn after 1, 10, 60, 180, and 1000 min (overnight). They were diluted with water and neutralized with NaOH solution to pH ~7. The aqueous solution was lyophilized, and a white solid was obtained. This solid was characterized by ¹H NMR and UV.

Deconvolution of UV–Vis Spectra. Applying "AutoFit Peaks II Second Derivative" function in PeakFit version 4.05, software from SPSS Inc. (AISN Software Inc.) allowed for deconvolution of the UV spectra and assignment of peaks due to the different isomers. The deconvolution process focused on the peaks in the 210–240 nm region of the methoxybenzene sulfonates (3) UV absorbance spectra. The software was allowed to fit the peaks within ± 1 nm of the wavelength (λ) for the model compound. The

same approach to deconvolution was used both for mixtures of compounds **3** and for *in situ* monolayer product analysis.

Monolayer Preparation and Characterization. For the preparation of siloxane-anchored SAMs, we used two kinds of substrates. Quartz slides were used for UV-visible spectroscopy and X-ray Photoelectron Spectroscopy (XPS) measurements (QSIL Quarzschmelze Ilmenau GmbH, microscope slides made of synthetic QUARZGLASS, class A acc. To DIN 58297, both sides polished). Silicon wafers (n-type, both sides polished) were used for attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, ellipsometry, and for wettability measurements (Silicon Sense Inc., Prime grade, phosphorus-doped $\langle 100 \rangle$, Fz, 515–535 μ m, > 1000 Ω).

Substrate Preparation. Quartz slides and silicon wafers were cut and then rinsed in chloroform, acetone and ethanol for 30 s each and dried in a filtered nitrogen stream. Samples were then immersed into piranha solution at 80 °C for 20 min. Samples were then washed three times with deionized water and dried in a filtered nitrogen stream. Piranha treatment of the silicon wafers yielded an oxide layer, which was typically measured by ellipsometry to be 1.8 ± 0.3 nm thick and a surface that was totally wetted by water. All the substrates were used within 0.5 h of having been cleaned/activated.

Deposition of Monolayer Films. Freshly cleaned silicon wafers or quartz slides were immersed into a silane solution in toluene $(25-50 \,\mu\text{L compound}/10 \,\text{mL solvent}, v/v)$ in a nitrogenpurged glovebox where ambient humidity was 35-40%. Deposition time was 3 h at room temperature. Samples were withdrawn from the deposition solution, rinsed with chloroform, sonicated in chloroform (20 min), and dried with a filtered N₂ flow.

Monolayer films were characterized using contact angle measurements, ellipsometry, XPS and ATR-FTIR as reported previously.⁶¹ UV–vis measurements of the SAM-coated quartz substrates used a Cary Model 100 spectrometer (in double beam transmission mode). Spectra were run against a reference sample of untreated quartz that had been cleaned in piranha solution. (70:30 concentrated H₂SO₄:H₂O₂ (30% v/v)). All samples were measured in the wavelength range of 190–400 nm. The observed absorption spectra were the sum of the monolayers on both sides of the quartz.

SAM Sulfonation. Transformations were carried out by placing the monolayer coated substrate (silicon wafers or quartz slides) in the reagent solution under the indicated reaction conditions. After the substrate was withdrawn from the reaction medium, it was cleaned by dipping into a series of four beakers of deionized water and dried with a stream of dry filtered nitrogen. The surface chemistry was assayed by FTIR, UV–vis, XPS, contact angle measurements, and/or ellipsometry. The different sulfonation conditions are detailed below.

Concentrated H_2SO_4 (at 5 and 25 °C). General Procedure. A dry 28 mL screw cap flat-bottom flask, charged with 20 mL of

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Table 1. Su	mary of Film	Thicknesses.	Wetting	Measurements	. and FTIR.	UV	. and XPS Data of SA	AMs
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_	terminal substituent	ellipsometric thickness [nm ±0.1]	PC model length [nm]	contact angle adv/rec/hys (deg)	FTIR absorption bands (cm^{-1})	$UV \lambda_{max} (nm)$	S(2p) peak in XPS (eV)
1	-H	1.8	1.9	91/82/9	2922/2852 (CH ₂ as/s) 3070, 3034 (Ar-H)	220	
2	-H	2.0	2.1	92/85/7	1601, 1589, 1497 (Ar ring) 2921/2852 (CH ₂ as/s) 3073 3034 (Ar-H)	220	
4	-SCOCH ₃	2.1	2.3	77/73/4	1601, 1589, 1497 (Ar ring) 2922/2852 (CH ₂ as/s) 1709 (C=O)	239	164
4ox	-SO ₃ H	2.3	2.1	completely wetted	1596, 1495 (Ar ring) 2923/2853 (CH ₂ as/s) 1599, 1500 (Ar ring)	233	169

concentrated H₂SO₄ (98%) and stoppered with a screw cap was maintained at the indicated temperature. The SAM coated substrate was added. The reaction times varied and ranged from 1 to 1140 min (19 h). After the indicated time, the substrate was removed from the sulfonation medium and cleaned as described above.

Concentrated $H_2SO_4 + TFAA$ at 10 °C.⁶² In a dry 50 mL round-bottom flask stoppered with a rubber septum and fitted with a magnetic stirring bar, under nitrogen atmosphere, TFAA (8.5 mL, 61 mmol) was added to the concentrated H₂SO₄ (1.5 mL, 28 mmol) with cooling at 10 °C. The mixture was stirred for 4 h, after which complete dissolution of H₂SO₄ was achieved; the solution appeared light brown. The SAM coated substrate was placed in a dry glass test tube under a nitrogen atmosphere, stoppered with a rubber septum. The reaction solution (3 mL for quartz slide, 10 mL for an ATR silicon prism) was transferred by syringe into the test tube and was maintained at 10 °C. The reaction times varied and ranged from 1 to 60 min. After indicated time, the substrate was removed and cleaned as described above.

Results

Preparation of Monolayer Forming Materials and Spectroscopic Model Compounds. The three isomeric monosulfonated anisoles (3a-c) were each obtained in pure form by oxidation. sulfonation or hydrolysis procedures, as described in the Supporting Information. On the basis of a procedure adapted from Pilyugin et al.,⁶³ the disulfonated model compound (3d) was synthesized in two steps: disulfonation of phenol in concentrated sulfuric acid,⁶⁴ followed by methylation of the free phenolate using dimethyl sulfate.

Trichlorosilane 2 was a known material and 1 was prepared in an analogous fashion using the one-carbon shorter alcohol. To separately study the first and the second sulfonation processes, trichlorosilane 4 was prepared, as an entry to an authentic, monosulfonated SAM. The somewhat circuitous synthesis described in Scheme 5 was necessitated by the competing nucleophilicities of the thiol and the hydroxyl groups. By protecting the thiol as a disulfide, selective ether formation was achieved. Disulfide reduction followed by acylation and hydrosilylation yielded 4. The thio-acetate provides for the in situ formation of sulfonate by oxidation.¹⁷ Alternative (unsuccessful) approaches to making an authentic monosulfonated SAM are described elsewhere.55

Trichlorosilanes 1, 2, and 4 were deposited on silicon and on quartz wafers. The characterization of the resulting films is summarized in Table 1. The UV-vis absorbance spectra of the SAMs are similar to those of the precursor compounds and of the anisolebased model compound (Figure 1). The measured thicknesses of the SAM1 and SAM2 are both within 0.1 nm of the calculated value for the extended conformation of the molecules as determined by PC Model (Serena Software). The FTIR data are consistent with those previously reported for SAM2 as an ordered monolaver.^{59,65} The FTIR spectra of SAM2 shows a somewhat larger methylene stretching intensity (as expected) relative to SAM1, along with a slight shift in peak position to lower wavenumbers (indicating a more ordered \hat{SAM}).⁵⁴ While the ether group has been reported to disrupt the local order of a monolayer^{66–68} due to changes in lateral van der-Waals interactions,^{69–72} we note that

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Figure 1. ATR-FTIR (left) and UV (right) spectra of monolayers prepared from phenyl ethers trichlorosilanes (SAM1 (solid line) and SAM2 (dotted line)).



Figure 2. Spectra of SAM based on compound 4 (S-4-(undec-10-enyloxy)phenyl ethanethioate) before (solid line) and after (dotted line) oxidation.

monolayers **SAM1** and **SAM2** seem to be more ordered than the corresponding thiol on gold SAM based on (11-phenoxyundecyl)mercaptan reported by Cavadas and Anderson.⁵⁸ Contact angle measurements for the phenyl ether monolayers are very similar to those of comparable non-oxygen containing monolayers (91 \pm 2° adv.),⁷³ suggesting that the phenyl group shields the oxygen from the interface. This is consistent with the report by Whitesides et al.^{67,68} that alkoxy groups with four or more carbon atoms effectively shield the oxygen atom from the interface.

The thio-acetate functional group at the outer surface of SAM4 was oxidized using saturated aqueous Oxone (2KHSO₅· KHSO₄·K₂SO₄) to provide the desired sulfonate functionalized monolayer SAM4ox (Scheme 4). This chemistry was followed by both ATR-FTIR and UV-vis spectroscopy (Figure 2). The SAMs show methylene signals in the FTIR at 2922 and 2852 cm⁻¹. The intensities of these peaks before and after oxidation are comparable. The carbonyl peak at 1709 cm⁻¹ disappeared upon oxidation. The peaks of the initial aryl thio-acetate are at 1596 and 1495 cm⁻¹ and after oxidation they appear at 1599 and 1500 cm⁻¹. In the UV spectra the peak at 239 nm shifts to 233 nm after the oxidation. These results are in good agreement with our findings for **3c**.

The oxidation of **SAM4** to **SAM4ox** is also supported by the advancing CA of 77° being replaced by a completely wetted film with CA close to 0°. Similarly, the XPS spectra (Figure 3) show a shift in the sulfur S(2p) binding energy from ~164 to ~169 eV, consistent with the starting thioacetate $(R^1-S-CO-R^2)$ becoming a sulfonic acid (R^1-SO_3H) . This is also in agreement with the published results for hexadecenyl thio-acetate SAM.¹⁷



Figure 3. XPS spectrum of S(2p) region in starting phenyl ethanethioate SAM (black) and phenyl sulfonate SAM (red).

Model Reactions. Sulfonation of Anisole. The sulfonation of anisole in solution can be followed by ¹H NMR. Product analysis based on the methoxy protons (Table 2) shows transient formation of the *ortho* and *para* derivatives (**3a** and **3c**) with no *meta* product (**3b**), ultimately leading to disulfonation (**3d**). This NMR data is shown together with UV analyses of the same reactions (obtained by curve resolution of the UV spectra of the reaction mixtures referenced to the spectra obtained from the model compounds). We note that the *ortho* isomer rapidly goes on

⁽⁷³⁾ Lee, S.; Puck, A.; Graupe, M.; Colorado, R., Jr.; Shon, Y. S.; Lee, T. R.; Perry, S. S. *Langmuir* **2001**, *17*, 7364–7370.

Table 2. Sulfonation of Anisole:	¹ H-NMR and UV-Vis Analyse	s of the Ratio of Products	3a:3c:3d as a Function o	of Time, Using F	our Different
	Rea	action Conditions ^a			

	ratio of sulfonated products 3a:3b:3d									
			concentra							
	5	°C	25	°C	85	°C	concentrated H ₂ S	O ₄ + TFAA 10 °C		
time, min	NMR	UV	NMR	UV	NMR	UV	NMR	UV		
1	24:63:13	27:60:13	8:58:34	9:61:30	10:64:26	13:61:25	0:3:97	0:0:100		
10	15:67:18	16:65:19	6:64:30	4:65:31	0:25:75	0:27:73	0:2:98	0:0:100		
60	12:74:14	14:70:16	2:67:31	1:65:33	0:2:98	0:2:98	0:3:97	0:0:100		
180	6:69:25	10:68:22	0:61:39	0:65:35	0:0:100	0:0:100				
1080	0.62.32	0.66.34	0.41.59	0.45.55						

^{*a*} Estimated errors are $\pm 2\%$.



Figure 4. ATR-FTIR (left) and UV-vis (right) spectra for the sulfonation of phenyl ether terminated SAM1 by concentrated H₂SO₄ at 5 °C.

to the doubly sulfonated material as indicated by the fact that, at some point, all of the reactions show only the *para* isomer and the disulfonated material. Also, under those reaction conditions where the first and second sulfonation processes can each be measured, the second sulfonation step is slower than the first.

The progressive shifts in the UV spectra of the reaction mixtures are sensible and these data nicely agree with the ¹H NMR experiments. At 5 °C, the early stage reaction mixture shows a peak at 230 nm. This is likely a combination of the 220 nm absorbance of the *ortho* isomer and the more intense 231 nm peak of the *para* isomer. As the reaction progresses, the peak position shifts to 232 nm – a combination of 231 nm (for the *para* isomer) and 234 nm for the disulfonated material. A fully sulfonated reaction mixture, as seen when the reaction is done at 85 °C or by using H₂SO₄ and TFAA shows the expected peak at 234 nm, consistent with producing the disulfonate **3d**.

The ¹H NMR analysis of the solution reactions (Table 2) allows us to validate the UV-based assay that will be used to determine the product distribution in the SAM analyses. Peak positions were assigned based on the model compounds' λ_{max} values (220 nm for *ortho* (**3a**) 231 nm for *para* (**3c**), and 234 nm for disulfonate (**3d**)). The reported ratio between the peaks obtained in the deconvolution also took into account their relative extinction coefficients (ε). The near perfect agreement (differences of < 2%) between the values obtained from integration of the NMR peaks and the UV deconvolution validate the UV analysis despite its broader peaks and their overlap.

In Situ Electrophilic Aromatic Sulfonation on Phenyl Ether SAMs. We studied SAM sulfonation using concentrated H_2SO_4 at 5 °C and at 25 °C and using a mixture of concentrated H_2SO_4 and TFAA at 10 °C. These reactions were monitored by a combination of ATR-FTIR and UV–vis spectroscopy. Sample spectra for SAM1 reacting with concentrated H_2SO_4 at 5 °C are shown in Figure 4.

The progress of the sulfonation reaction was monitored *in situ* by UV-vis spectroscopy for times up to 1140 min. Sulfonation using $H_2SO_4 + TFAA$ was so fast that it was monitored for only 60 min. Sulfonation immediately gave rise to changes in UV and FTIR spectra and wetting measurements with CA of ~0°.

The main UV absorption shifted from 220 nm for the asdeposited SAM to $\lambda_{max} = 235$ nm. This was accompanied by a slight decrease in peak intensity, consistent with increasing amount of disulfonate having a smaller ε than the *para* sulfonate. In the region of 270 nm, the three minor peaks of the initially deposited phenyl ether SAM disappear. Since these peaks are relatively small and each of the model compounds shows 2–3 peaks in this region, no attempt was made to quantitate them by deconvolution.

XPS confirms the incorporation of sulfonate groups into the monolayer with a peak at ~169 eV for the oxidized sulfur S(2p) electrons.^{54,55} These results also are consistent with double sulfonation as the S/C ratio ultimately observed is considerably higher than for the alkylbenzene system with its monosulfonation.⁵⁴

The FTIR of the originally deposited SAM shows peaks for the aromatic rings at 1601, 1588, and 1497 cm⁻¹. As sulfonation proceeds they shift to 1598 and 1581 cm⁻¹ and the peak at 1497 cm⁻¹ disappears. On the basis of the model compounds (3), the peak at 1581 cm⁻¹ corresponds to the *para*-sulfonated phenyl ether while the peak at 1598 cm⁻¹ reflects a combination of the *para*-sulfonated and the disulfonated materials at 1601 and 1596 cm⁻¹, respectively. When the reaction is complete only the peak at 1596 cm⁻¹ is seen.

The FTIR spectra also suggest that introducing the sulfonate groups into the well-packed SAM causes some disorder. The antisymmetric and symmetric $-CH_2$ - stretching modes of the sulfonated SAM are at 2925 and 2854 cm⁻¹, respectively. They are shifted and broadened (32 ± 3 cm⁻¹ fwhm) relative to the initially deposited monolayer (2922 and 2852 cm⁻¹, 29 ± 3 cm⁻¹ fwhm).



Figure 5. UV-vis peak deconvolution of the sulfonation of **SAM1** using concentrated H_2SO_4 at 5 °C after (A) 1 min, (B) 150 min and (C) 330 min. Key: (\bigcirc) experimental spectra; ($\blacksquare, \blacktriangle, \blacklozenge$) resolved components of *ortho* sulfonate, *para* sulfonate, and disulfonate respectively ($R^2 > 0.99$, solid line).

The FTIR signals of the sulfonate groups could not be seen due to the silicon substrate blocking the spectral window below \sim 1480 cm⁻¹.

Deconvolution and Product Distribution Determination for SAM Sulfonation. A typical UV absorption spectrum of sulfonated aryl terminated SAM films shows a broad absorbance band that can, by reference to the model compounds described above, be deconvoluted as a possible mixture of *ortho* sulfonated, *para* sulfonated, and disulfonated products. This analysis makes two assumptions: (1) based on its absence in the model reactions, the possibility of a *meta* isomer product was ignored; (2) the extinction coefficients of the components of the sulfonated SAMs are comparable to those of the small molecule model compounds (3) and environment induced changes are likely to be of comparable proportions for all isomers.

Figure 5 shows an example of deconvoluted spectra for the sulfonation of SAM1 using concentrated H₂SO₄ at 5 °C. All the deconvoluted spectra show the nearly instantaneous appearance of initially formed ortho and para isomers. These steadily disappear in favor of increasing amounts of disulfonated material. The ratio of sulfonated products was determined from the peaks at 221, 230, and 238 nm for the ortho sulfonated, para sulfonated, and disulfonated products, respectively. The SAM environment shifted these values from the authentic absorptions of 220, 231, and 234 nm, respectively. The 4 nm shift for the disulfonated material may indicate that it is mostly monoprotonated on the monolayer surface while the model compound in solution was completely doubly ionized. Cerfontain reported⁷⁴ that increasing sulfuric acid concentration induced a bathochromic shift in the UV absorption of arene-sulfonic acids due to protonation of the sulfonate, while the effect of changes in ionization on their extinction coefficients is less than 5%. The UV spectrum of compound 3d in concentrated H_2SO_4 shows $\lambda_{max} = 240$ nm. Thus, the shift from 234 to 238 nm is reasonable.

Using the extinction coefficients measured for the model compounds, the Beer–Lambert relationship allowed the determination of the molar concentration of the *ortho* sulfonate, *para* sulfonate, and disulfonated materials. Since product distributions calculated based on peak amplitude or peak area are within < 2% of each other, they are averaged.⁵⁴ The product ratios obtained in the sulfonations of **SAM1** and **SAM2** are summarized in Table 3. Importantly, both SAMs afford the same final product mixtures

Table 3. Product Distribution for Maximally Sulfonated Phenyl Ether SAMs

	product distribution (%)		
conditions	SAM1	SAM2	
concentrated H ₂ SO ₄ 5 °C	22 0-	19 <i>o</i> -	
	19 <i>p</i> -	20 p-	
	59 di-	61 di-	
concentrated H ₂ SO ₄ 25 °C	19 <i>o</i> -	18 <i>o</i> -	
	18 p-	22 p-	
	63 di-	60 di-	
concentrated H ₂ SO ₄ + TFAA 10 °C	21 <i>o</i> -	20 o-	
	20 p-	20 p-	
	59 đi-	60 đi-	

Scheme 6. Sulfonation of Phenyl Ether and Its Rate Constants



($\sim 20\%$ ortho sulfonation, $\sim 20\%$ para sulfonation, and $\sim 60\%$ disulfonation), regardless of the reaction conditions and despite the fact that the reaction with TFAA/H₂SO₄ was over in a few minutes while the sulfonations in sulfuric acid took hours to go to completion.

Kinetic Analysis of SAM Sulfonation. The kinetics of the sulfonation of the phenyl ether SAMs is complicated by the fact that the initially formed *ortho* and *para* isomers react further to produce doubly sulfonated molecules. Each reaction can be treated as pseudofirst order and the overall scheme is that of two consecutive first-order reactions that take place in parallel (Scheme 6). Each of the rate constants indicated herein is actually the combination of multiple forward and reverse processes.

The rate of disappearance of the aryl molecule ([ArH]) can be expressed as:

$$[\operatorname{ArH}] = [\operatorname{ArH}]_{0} e^{-(k_{0}+k_{p})t}$$
(1)

The rate equations for the *ortho* and *para* isomers include both their formation $(k_0 \text{ or } k_p)$ and their subsequent consumption to

⁽⁷⁴⁾ Cerfontain, H.; Schnitger, B. W. Recl. Trav. Chim. Pays-Bas 1972, 91, 199-208.



Figure 6. Sulfonation product distribution for SAM1 (left) and SAM2 (right) using concentrated H₂SO₄ at 5 °C: (\blacksquare , \blacktriangle , \blacklozenge) *ortho* sulfonation, *para* sulfonation, and disulfonation, respectively.

make the disulfonate (k_{od} and k_{pd}):

$$\frac{\mathrm{d}[ortho]}{\mathrm{d}t} = k_{\mathrm{o}}[\mathrm{ArH}] - k_{\mathrm{od}}[ortho]$$
$$= k_{\mathrm{o}}[\mathrm{ArH}]_{0}\mathrm{e}^{-(k_{\mathrm{o}}+k_{\mathrm{p}})t} - k_{\mathrm{pd}}[ortho]$$
(2)

$$\frac{\mathrm{d}[para]}{\mathrm{d}t} = k_{\mathrm{p}}[\mathrm{ArH}] - k_{\mathrm{pd}}[para]$$
$$= k_{\mathrm{p}}[\mathrm{ArH}]_{0}\mathrm{e}^{-(k_{\mathrm{o}}+k_{\mathrm{p}})t} - k_{\mathrm{pd}}[para]$$
(3)

These are nonhomogenous differential equations. The resolution of these equations and placing starting conditions (at t = 0 both [*ortho*] and [*para*] = 0) gives:

$$[ortho] = \frac{k_{\rm o}[{\rm ArH}]_0}{k_{\rm od} - (k_{\rm o} + k_{\rm p})} \left[e^{-(k_{\rm o} + k_{\rm p})t} - e^{-k_{\rm od}t} \right]$$
(4)

$$[para] = \frac{k_{\rm p} [{\rm ArH}]_0}{k_{\rm pd} - (k_{\rm o} + k_{\rm p})} \left[e^{-(k_{\rm o} + k_{\rm p})t} - e^{-k_{\rm pd}t} \right]$$
(5)

The doubly sulfonated material is obtained from the sulfonation of the *ortho* and *para* isomers. Thus, its rate expression may be written as:

$$\frac{\mathrm{d}[\mathrm{d}i]}{\mathrm{d}t} = k_{\mathrm{od}}[ortho] + k_{\mathrm{pd}}[para] \tag{6}$$

By incorporating equations eq 4 and eq 5 into eq 6 we get:

$$\frac{d[di]}{dt} = \frac{k_{od}k_{o}[ArH]_{0}}{k_{od} - (k_{o} + k_{p})} \left[e^{-(k_{o} + k_{p})t} - e^{-k_{od}t} \right] \\ + \frac{k_{pd}k_{p}[ArH]_{0}}{k_{pd} - (k_{o} + k_{p})} \left[e^{-(k_{o} + k_{p})t} - e^{-k_{pd}t} \right]$$
(7)

The resolution of this differential equation leads to

$$[di] = [ArH]_{0} \left\{ 1 + \frac{k_{o}}{k_{od} - (k_{o} + k_{p})} \left[e^{-k_{od}t} - \frac{k_{od}}{k_{o} + k_{p}} e^{-(k_{o} + k_{p})t} \right] + \frac{k_{p}}{k_{pd} - (k_{o} + k_{p})} \left[e^{-k_{pd}t} - \frac{k_{pd}}{k_{o} + k_{p}} e^{-(k_{o} + k_{p})t} \right] \right\}$$
(8)

Deconvoluting the UV spectra collected during *in situ* sulfonation enables us to quantify the relative amounts of *ortho* sulfonates, *para* sulfonates, and disulfonates present at each time point. This analysis showed that the formation of *ortho*-sulfonated product is initially favored in **SAM1** (Figure 6, left), while formation of *para*-sulfonated product is initially favored in **SAM2** (Figure 6, right). As the reaction proceeds and the amount of disulfonated material steadily increases, the ratio of the *para* and *ortho* isomers approaches \sim 1:1 in both cases.

Plotting the data collected as a function of time (Figure 6) allowed us to extract rate-constants for the production of doubly sulfonated material from *ortho*- and *para*-sulfonated phenyl ether monolayers, by fitting curves with a trend line having the general formula presented in eq 9 (adopted from the expressions for concentrations of *ortho* (eq 4) and *para* (eq 5)).

$$y = \frac{k_1}{k_3 - (k_1 + k_2)} \left[e^{-(k_1 + k_2)t} - e^{-k_3 t} \right]$$
(9)

 k_1 and k_2 are the rate constants for the monosulfonation reaction. The rate of the second sulfonation (k_3) calculated from the *ortho* curves (analogous to that found in Figure 6) is k_{od} , while the *para* curve gives the rate of conversion of *para* sulfonate to the doubly sulfonated material (k_{pd}).

The rate constants for the initial formation of the *ortho* and *para* derivatives were difficult to determine since by the time we could make our first measurements (after ~0.5 min), there were already substantial amounts of doubly sulfonated material. In theory, our fitted trend line (eq 9) should provide us with rate constants for the monosulfonation reactions. In practice, however, almost any values for k_1 and k_2 give a good fit as long as they are much larger than the value of k_3 (rate of second sulfonation reaction, eq 9). All we can say is that the rate constants for the formation of the *ortho* and *para* isomers are several orders of magnitude larger than the initial rates of conversion of each of the isomers to the doubly sulfonated material.

It should be noted, that any fitting procedure used to determine rate constants for the entire course of the reaction failed. Reasonable fits could only be obtained for times in which the amount of doubly substituted material generated was no more than 40-50%. From then on, the sulfonation reaction slows drastically and effectively stops at 60%.

By dividing the sulfonation reaction into "early" and "late" stages^{54,55} we can extract useful estimates (Table 4). Clearly, incorporation of the second sulfonate group into an organized monolayer is more difficult and reaction rates are significantly slower. By calculating a separate pseudofirst order rate constant for the earlier stage of the reaction (up to 30% of doubly sulfonated material), we improved the fit to $R^2 = 0.97-0.99$, though we could still only determine the rate of conversion of the

Table 4. Rate Constants for the Formation of Doubly Sulfonated Material in SAM1 and SAM2 from the Graphically Fitted Values of k3

			rate constant $k (\min^{-1})$					
		H ₂ SO	4 5 °C		H ₂ SO ₄ 25 °C			
		up to 30%	up to 50%	up to 30%	up to 50%			
SAM1	k _{od}	-	$1.85 \times 10^{-3} (R^2 = 0.99)$ $1.47 \times 10^{-3} (R^2 = 0.99)$	-	$3.55 \times 10^{-3} (R^2 = 0.99)$ 2 68 × 10^{-3} (R^2 = 0.99)			
SAM2	$k_{\rm od}$ $k_{\rm pd}$	$4.73 \times 10^{-3} (R^2 = 0.98) 4.28 \times 10^{-3} (R^2 = 0.97)$	$\begin{array}{c} 1.47 \times 10^{-3} \ (R^2 = 0.91) \\ 2.41 \times 10^{-3} \ (R^2 = 0.91) \\ 2.54 \times 10^{-3} \ (R^2 = 0.94) \end{array}$	-	$\begin{array}{c} 2.00 \times 10^{-3} \ (R^2 = 0.94) \\ 2.53 \times 10^{-3} \ (R^2 = 0.97) \end{array}$			

monosulfonate to disulfonate. Even so, rates of the "early" stage reaction could only be determined for **SAM2** under the mildest sulfonating conditions since in all other cases the reaction time was too short to allow an accurate determination. Finally, any attempt to understand this data must recognize that the slowing of the sulfonation could, in principle, arise from a decrease in the rate of conversion of mono to disulfonated material or from an increase in the rate of a reverse process wherein one of the sulfonic acid groups is lost in the rate-determining step.⁷⁵

Sulfonation of Authentic *p*-(Undecyloxy)benzenesulfonic Acid (SAM4ox). We have prepared SAMs of isomerically pure *p*-(undecyloxy)benzenesulfonic acid (SAM4ox) by oxidizing the corresponding thioacetate (SAM4) (Scheme 4). In principle, this system could directly measure a value for k_{pd} . In fact, no further sulfonation occurred and no doubly sulfonated material could be detected—the observed spectra remained that of the *para*-sulfonated material. This observation will be discussed below.

Discussion

The alkylbenzene⁵⁴ and phenyl ether SAMs (reported herein) are of sufficiently different reactivity so as to allow us to address different aspects of the affect of the monolayer on the interfacial chemistry. Also, the SAM substrates are sufficiently ordered such that modest changes in structure can change the way in which monolayer constraints⁵² influence the reactions.^{76–78}

FTIR and contact angle analysis of the comparison between the alkylbenzene⁵⁴ and the present phenyl ether data suggests that replacing a methylene with an ether oxygen exerts only a small influence on the packing and wetting properties of the SAM, despite its large impact on the electronic properties and reactivity of the aryl ring. Phenyl ethers SAMs are sufficiently activated toward electrophilic aromatic substitution that using concentrated H₂SO₄ at 5 °C left no unreacted phenyl ether after 1 min of reaction while under these same conditions, the alkylbenzene SAMs showed significant amounts of unreacted material for times up to 180 min.⁵⁴ This enhanced reactivity is consistent with our model reactions on anisole (Table 2) and with literature reports that the sulfonation of anisole with concentrated sulfuric acid produces 4-methoxybenzene-1,3-disulfonic acid⁵⁶ with a half-life of less than 1 min at room temperature.^{57,79}

We also note that our solution studies and those in the literature both suggest that the *ortho* monosulfonated isomer forms disulfonate faster than its *para* isomer counterpart. This is consistent with the SAM results reported in Table 4. For SAM1, k_{od} is consistently bigger than k_{pd} . This is also true for SAM2, except for the later stage of the reaction at 5 °C where the values are comparable and the R^2 values are poorer.

Scheme 7. Proposed Mechanism for Sulfonation in Concentrated Sulfuric Acid⁷⁵

(1)
$$\operatorname{ArH} + \operatorname{H}_2 \operatorname{S}_2 \operatorname{O}_7 \xrightarrow{k_I} \operatorname{Ar}^+ \operatorname{SO}_3^- + \operatorname{H}_2 \operatorname{SO}_4$$

(2) $\operatorname{Ar}^+ \operatorname{SO}_3^- + \operatorname{H}_3 \operatorname{O}_4^- \xrightarrow{k_2} \operatorname{Ar}_3 \operatorname{SO}_3^- + \operatorname{H}_2 \operatorname{SO}_4$

(3) $\operatorname{ArSO}_3^- + \operatorname{H}_3O^+ \longrightarrow \operatorname{ArSO}_3H + \operatorname{H}_2O$

Sulfonation of the phenyl ether SAMs is most clearly different from the solution model compounds in that its final product distribution is $\sim 20\%$ ortho sulfonate, $\sim 20\%$ para sulfonate, and $\sim 60\%$ disulfonate for both SAMs and under all reaction conditions. The fact that this reaction does not go to completion despite an overwhelming excess of sulfonating agent must be a reflection of a monolayer induced confinement effect, presumably based on a combination of charge and steric effects.

The rate-determining step of the first sulfonation in concentrated sulfuric acid is the conversion of the σ -complex into the corresponding sulfonate^{75,80} (Scheme 7). The comparable process in the second sulfonation would, upon loss of a proton, yield doubly sulfonated material, while loss of SO₃, would revert to the monosulfonated material. This loss of SO₃ may be increasingly favored as sulfonation progresses due to the additional crowding that would be induced into an organized monolayer structure by bulky sulfonate groups. It is also possible that electrophile access at a heavily sulfonated surface is more difficult and this suppresses the second sulfonation process.^{8,33,48}

Support for these explanations can be found by analogy to reports in the literature on solution sulfonation. A substantial decrease in sulfonation reaction rates is observed as one reacts increasingly more crowded substrates.⁸¹ It is also possible that in some conformations of the σ -complex, the hydrogen sulfate that may be needed to remove the proton and rearomatize the ring, cannot approach the proton to be removed.⁸⁰ It has also been suggested that sulfonation can be disfavored by the higher energy transition state (due to steric strain) involved in bringing the sulfonate group into the plane of the phenyl ring.⁸⁰

Sulfuric acid sulfonation of the alkylbenzene SAMs varied somewhat for reaction at the *ortho* or *para* positions and varied with the length of the alkyl tether. Nevertheless, these rates were all in the range of $0.01-0.27 \text{ min}^{-1}$ at 5 °C and $0.3-1.2 \text{ min}^{-1}$ at 25 °C. For the phenyl ether SAMs, initial monosulfonation proceeded so rapidly that precise rate constants could not be obtained. We could only estimate k_o and k_p to be 5–25 min⁻¹ (eq 9).⁸² This is a rate enhancement of ~2 orders of magnitude relative to the alkylbenzene system.

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Figure 7. Ring orientations for SAM1 and SAM2 by analogy to Cavadas and Anderson. 58

The second sulfonation of the phenyl ether substrates is expected to be slower than the first sulfonation at least in part since the monosulfonated molecule is less electron-rich than the original phenyl ether. Despite this slowing, the initial stages of the second sulfonation remain roughly first order. The drastic decrease in the rate of this reaction starts to be manifest when 40-50% doubly sulfonated material has been formed. Not surprisingly, the second sulfonation of the para isomer is more seriously suppressed due to the steric hindrance involved in incorporating a sulfonate group in an ortho position (as was seen in the monosulfonation of alkylbenzene SAMs^{54,55}). However, reaction at the *para* position of the initially formed o-substituted compound also stops. As suggested above, this may be attributable to a decrease in the reaction rate of the forward reaction $(k_1 \text{ or } k_2)$ or an increase in the rate at which the σ -complex reverts to the monosulfonated product (k_{-1}) . The end result is a leveling off of the product distribution at the interface with an *ortho/para* ratio of about 1.

In general, the reactions on the SAMs are slower than the reactions in solution. Also, the rate at which the *ortho* isomer is converted to doubly sulfonated material is larger than for the *para* isomer. This is sensible since it is likely that it is easier to access the *para* position than the *ortho* position of a tethered phenyl ring within the SAM surface.

The phenyl rings in SAM1 and SAM2 are attached to the surface by tethers that differ by one methylene unit. When comparing the structures of these SAMs, we note that films prepared from 2 are more ordered (antisymmetric $-CH_2-$ vibration at 2921–2922 cm⁻¹) than the films prepared from 1 (antisymmetric $-CH_2-$ vibration at 2922–2923 cm⁻¹). Any difference in reaction rate between the two is nevertheless small (Table 4). The only significant difference between the two tethers seems to be in the monosulfonated isomer formed in the early stage of the reaction. Figure 6 shows how the *ortho* isomer predominates in the monosulfonated product mixture for SAM1 and the *para* isomer is dominant for SAM2 (before the ultimate formation of a 1:1 mixture in both systems).

Cavadas and Anderson⁵⁸ report the reflection-absorption infrared spectroscopy (RAIRS) of 11-phenoxyundecyl mercaptan SAMs on gold. These spectra show terminal phenyl groups that have their C1-C4 ring axis aligned with the surface normal (as reflected in the strong intensities of the absorptions at 1601 cm⁻¹). By analogy, the C1-C4 ring axis in **SAM2** should be only slightly tilted from the surface normal. When combined with the known variation in ring orientation as a function of chain length shown for alkylbenzenes,⁷³ **SAM1** should have more substantially tilted phenyl rings (Figure 7). Thus, it is sensible that in the early stages of the sulfonation reaction (as per Figure 6 and the tables in the Supporting Information) **SAM2** shows a preference for the formation of the *para* monosulfonate, while **SAM1**, where the phenyl rings are more tilted and the *ortho* positions are more exposed, allows for more *ortho* monosulfonation. The above explanation is consistent with the variation in product distribution that we previously reported for the alkylbenzene system.⁵⁴ The RAIRS data reported by Lee et al.⁷³ and Cavadas and Anderson⁵⁸ showed that SAMs of 12-phenyldodecyl mercaptan on gold have terminal phenyl groups with the C1–C4 ring axis substantially tilted from the surface normal. It was sensible to suggest that alkyl-tethered SAMs with one less carbon in their polymethylene chain would be only slightly tilted from the surface normal. The product distributions reported for the sulfonation of alkylbenzene SAMs⁵⁴ were consistent with the idea that when the C1–C4 ring axis was more tilted there was a distinct preference for *ortho* isomer formation, while less tilted rings increased *para* sulfonation.

Attempted Sulfonation of p-(Undecyloxy)benzenesulfonic Acid SAMs. The observation that authentic *p*-(undecyloxy) benzenesulfonic acid SAM does not further sulfonate is striking. The evolution of product mixtures seen in both SAM1 and SAM2 require that some initially formed *para*-sulfonate goes on to disulfonate. We therefore suggest that the initial stages of the sulfonation of the aryl terminated SAMs introduce some disorder. This is consistent with the shift in the vibrational modes of the methylenes from 2921 to 2925 cm^{-1} that we described above for monolayers of SAM1 and SAM2. The initially formed mix of ortho and para monosulfonated materials promote a disordering that presumably facilitates the second sulfonation. On the other hand, the aryl thioacetate precursor of the authentic para sulfonate is moderately well ordered (Figure 4) and this order is not undermined by the oxidation of the thioacetate to the sulfonate.

It seems that the relatively good order within the authentic para sulfonate SAM strongly inhibits reaction at the less accessible ortho position and effectively prevents its sulfonation. This is consistent with precedent that well-ordered monolayers can block penetration of guest molecules into the monolayer and that the degree of order and the immediate environment around a functional group can strongly affect its reactivity.³² Reagent penetration may be sterically impeded by monolayer packing and/or by increased intramonolayer hydrogen bonding in the ordered array. This data also suggests that disordered monolayers formed by the first sulfonation of SAM1 or SAM2 exist in a liquid-like phase that is more easily permeable than would be the case for a well-packed quasicrystalline monolayer. Furthermore, consistent with the picture in Figure 7, the C1-C4 ring axis of the p-(undecyloxy)benzenesulfonic acid SAM should be aligned with the surface normal. This orientation of the phenyl ring makes the ortho positions particularly inaccessible.

Summary

We have demonstrated the use of sulfonation to convert a relatively inert, low free-energy surface SAM into a hydrophilic, negatively charged SAM by the introduction of sulfonate functionality. Using curve resolution on *in situ* collected data, we can determine reaction kinetics and product distributions within the monolayer environment. Changes in SAM structure as the reaction progresses can be detected and differences in the orientation of the terminal phenyl ring as a function of the tether by which it is attached to the substrate seem to influence the initial isomer distribution produced in the reaction. The sulfonation is slowed by changes in the interfacial environment such that sulfonation stops completely after 60% disulfonation due to charge repulsion and/or steric hindrance. This ultimately limits the degree to which *in situ* sulfonation can be used to create ordered interfaces with

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particularly high negative charge density. It is an interesting demonstration of what seems to be a combination of steric and Coulombic constraints imposed by the structure of the closepacked monolayer.

Acknowledgment. Financial support of this work by the Israel Science Foundation, the US-Israel Binational Science Foundation, the Minerva Center for Biomaterial Interfaces, and the Edward and Judy Steinberg Chair in Nanotechnology at Bar-Ilan University, is gratefully acknowledged. **Supporting Information Available:** (a) Text giving syntheses and spectroscopic characterizations of compounds 1, 2, **3a**, **3b**, **3c**, **3d**, and **4**, (b) figures showing representative FTIR and UV-vis spectra of the model compounds **3**, (c) figures showing ATR-FTIR and UV-vis spectra of the *in situ* sulfonation reaction of **SAM2** using concentrated H_2SO_4 at 5 °C, and (d) data tables obtained from the deconvolution of the UV spectra used to determine SAM product distribution. This material is available free of charge via the Internet at http://pubs.acs.org.