

The Structure of Self-Assembled Monolayers of Alkylsiloxanes on Silicon: A Comparison of Results from Ellipsometry and Low-Angle X-ray Reflectivity

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Received October 12, 1988

Abstract: The thicknesses of C10–C18 alkylsiloxane monolayers on silicon–silicon dioxide substrates have been measured with ellipsometry and low-angle X-ray reflection. Although, for any given sample, thicknesses measured by the two methods agree to within experimental error, ellipsometric measurements are systematically larger by approximately 2 Å. This difference may result from variations in the sensitivity of the two techniques to the structure of the interface between silicon dioxide and the alkylsiloxane monolayer. The X-ray reflectivity measurements provide evidence that these organic monolayers do not build up as island structures and demonstrate that the approximate area projected by each alkyl group in the plane of the monolayer is $\sim 21 \pm 3 \text{ \AA}^2$. Preliminary studies indicate that this technique can be used to follow the changes in the structure of a monolayer which result from chemical transformations. The influence of damage that is induced by X-ray radiation on these measurements is discussed.

This paper describes the use of ellipsometry and low-angle X-ray reflectivity to characterize monolayers prepared by reaction of alkyltrichlorosilanes with the surface silanol groups of silicon bearing a hydrated native oxide. Our primary objective was to compare estimates of the thicknesses of these films obtained by using these two techniques. Ellipsometry has been employed extensively for the measurement of the thicknesses of thin organic films.^{1–5} X-ray reflectivity is just beginning to be used for this purpose.^{6–11} Agreement between ellipsometry and X-ray reflectivity would help to validate both techniques. A secondary objective was to examine the structural order of these self-assembled alkylsiloxane monolayers. As part of this work, we have attempted to generate monolayers that have a variation in electron density along the normal to the substrate surface. The intensity of the X-rays reflected from such samples is sensitive to this type of change in electron density.^{6,12} The determination of the electron distribution in films ostensibly having variations in electron density along the *z* axis would provide one direct measure of order in these systems.

Previous studies have attempted to verify the accuracy of ellipsometry in determining the thicknesses of organic monolayers. For Langmuir–Blodgett monolayers, estimates of thickness by ellipsometry, isotopic labeling,^{13,14} and surface pressures¹⁵ are in agreement. These experiments depended, however, on comparisons of complete and partial monolayers and demonstrated only that the thickness of a monolayer as measured by ellipsometry correlates with the number of molecules per unit area in that monolayer and their length. We have reached a similar conclusion when correlating the ellipsometric thicknesses of monolayers prepared from a homologous series of alkyltrichlorosilanes with the relative intensities of carbon and silicon observed in X-ray photoelectron spectroscopy (XPS).¹⁶ This conclusion has also been reached in related experiments that utilized monolayers of alkyl thiols adsorbed on gold films.¹⁷

Against the background of these earlier studies, we had two reasons to conduct a comparison of results from ellipsometry and X-ray reflection. First, these previous studies did not directly measure the thickness of the monolayers. Second, they examined Langmuir–Blodgett, rather than self-assembled, monolayers.

The self-assembled monolayers used in this work were prepared by placing a silicon–silicon dioxide (Si/SiO₂) substrate in a solution

containing an alkyltrichlorosilane (RSiCl₃).¹⁸ The Si–Cl bonds react with silanol groups¹⁹ and adsorbed water²⁰ present on the surface of the silicon dioxide and form a network of Si–O–Si bonds of undefined structure.²¹ The resulting monolayers are bound covalently to the substrate and are stable. XPS reveals that no chlorine remains in them.¹⁶ The density of surface silanol groups on the native oxide is only ~ 1 per 20 Å².^{22,23} This density is approximately equal to the surface density of R groups within the monolayer (see below). The remaining Si–Cl bonds of the RSiCl₃ groups apparently react with water²⁴ and form Si–O–Si and/or Si–OH moieties.

Ellipsometry and low-angle X-ray reflection are both optical

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- (24) Water seems to be necessary for the formation of alkylsiloxane monolayers. When prepared in a dry nitrogen atmosphere, the preparation of a complete monolayer requires longer times of immersion (~ 5 h) than when the process is performed in the ambient laboratory environment (~ 30 min).

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techniques based on the reflection of light from interfaces. Although these two techniques are described using the same theoretical treatment—Fresnel's equations for the reflection of light²⁵—they measure different properties of the light reflected from an interface. In addition, the wavelengths of the light used here in ellipsometry ($\lambda = 6328 \text{ \AA}$) and X-ray reflection ($\lambda \approx 1.5\text{--}1.7 \text{ \AA}$) differed by more than a factor of 10^3 . The two techniques are also sensitive to different facets of interfacial structure.

Results

Preparation of Monolayers. We prepared alkylsiloxane monolayers on silicon–silicon dioxide (Si/SiO₂) substrates by reaction with alkyltrichlorosilanes using techniques similar to those described previously.^{16,18,26} Because the measurement of X-ray reflection requires large, flat samples, the silicon substrates for these studies were significantly larger ($2.5 \times 7.5 \text{ cm}$) and, in general, thicker (0.125 in.) than those used previously.²⁷ Some samples were, however, prepared on thin (0.015 in.) substrates.²⁸ We examined monolayers prepared from saturated alkyltrichlorosilanes ($\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{CH}_3$, $n = 9, 11, 14, 15, 17$), from 16-heptadecyltrichlorosilane (HTS, $\text{Cl}_3\text{Si}(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$), and from a fluorinated silane ($\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$).

Ellipsometry. The theory of ellipsometry has been discussed in detail by others.^{1,29} Here we summarize certain important details and assumptions of the method.

Ellipsometry analyzes the reflection of elliptically polarized light from an interface separating two media with different indices of refraction. This elliptically polarized light can be represented as the sum of two components, one in the plane of incidence of the light (p polarization), the other perpendicular to this plane (s polarization). Upon reflection, the amplitude and phase of each of these components is altered, resulting in a change in the overall polarization and amplitude of the light wave. These changes in amplitude and phase are represented by the Fresnel reflection coefficients for the p and s polarizations, r_p and r_s . Ellipsometry measures the ratio of these coefficients, ρ . The standard relationships between ρ and the measured analyzer (A) and polarizer (P) angles are summarized in eq 1–3.^{1,29} The angle ψ represents

$$\rho = r_p/r_s = \tan \psi \exp(i\Delta) \quad (1)$$

$$\psi = A \quad (2)$$

$$\Delta = 2P + \pi/2 \quad (3)$$

the ratio of the changes in amplitude for the s and p polarizations of light upon reflection from an interface. The angle Δ is the difference in the phase shifts that are experienced by each polarization upon reflection.

In order to use ellipsometry to determine the thickness of a monolayer supported on a substrate, one must compare data obtained from the monolayer–substrate system with those from the uncoated substrate.³⁰ This comparison is straightforward, but differences between the substrate in coated and uncoated form may skew the ellipsometric results. Clean silicon–silicon dioxide has a high surface free energy and, therefore, a high affinity for both water and organic contaminants. Organic monolayers terminating in methyl and vinyl groups have low interfacial free

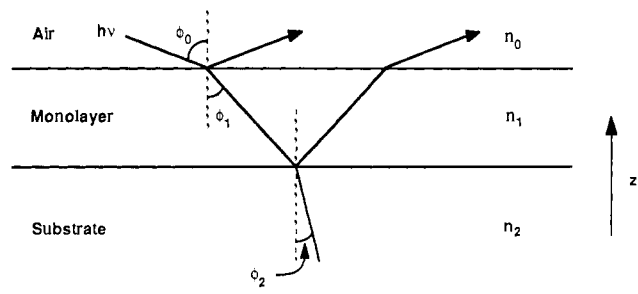


Figure 1. Two-layer model used for ellipsometry. The silicon substrate has refractive index n_2 , the monolayer has refractive index n_1 , and the ambient air has refractive index n_0 . The interfaces between each layer are assumed to be perfectly sharp. For the alkylsiloxane monolayers on silicon, n_2 is ~ 3.8 , n_1 is ~ 1.45 , and n_0 is assumed to be 1. The incident angle of the laser light, ϕ_0 , is 70° . The angles of refraction, $\phi_1 \approx 40^\circ$ and $\phi_2 \approx 15^\circ$, are given by Snell's law ($n_1 \sin \phi_1 = n_2 \sin \phi_2$).

energies and resist contamination.³¹ If contamination of the bare Si/SiO₂ substrate were significant, we would expect that the thicknesses of the monolayers as measured by ellipsometry would be too small. We have found that the thicknesses of these *n*-alkylsiloxane monolayers correspond very closely to those which we expect for a *trans*-extended chain oriented perpendicular to the surface:¹⁶ that is, to the largest plausible thickness. A *trans*-extended chain is in agreement with infrared measurements of chain geometry.³² We conclude, on the basis of these two lines of evidence, that contamination does not appear to affect the ellipsometric results in these systems.³³

The conventional interpretation of the ellipsometric data is based on a model consisting of parallel interfaces separating air, the alkylsiloxane monolayer, and the substrate (Figure 1). The effectively infinitely thick substrate has a refractive index n_2 , the monolayer has a uniform refractive index n_1 , and the ambient atmosphere has refractive index n_0 (which is assumed to be 1). Since the silicon substrates have a native surface oxide layer,^{34,35} a three-layer model might, in principle, provide a more accurate representation of the structure of the monolayer. In practice, we have used a two-layer model and have measured a single effective refractive index for the substrate that combines contributions from the bulk silicon and the surface oxide.³⁶ Although we assume that the two interfaces, monolayer–substrate and air–monolayer, are perfectly smooth, theoretical and experimental studies suggest that, for ellipsometry, roughness has little effect on the measured thickness of the monolayer.^{37–39}

Ellipsometry can, in principle, determine both the thickness and the refractive index of a monolayer. For the very thin ($<50 \text{ \AA}$) films examined here, it is not, however, possible to determine both of these quantities simultaneously.⁴⁰ We must, therefore, assume a value for one of them before calculating the other. We have

(31) The contact angles of water and hexadecane on the bare substrate were $\theta_a^{\text{H}_2\text{O}} \approx 0^\circ$; $\theta_a^{\text{HD}} \approx 0^\circ$. The contact angles for monolayers prepared from octadecyltrichlorosilane (OTS) were $\theta_a^{\text{H}_2\text{O}} = 112^\circ$; $\theta_a^{\text{HD}} = 42^\circ$.

(32) Infrared spectroscopy using polarized radiation suggests that these monolayers are oriented nearly perpendicular to the surface (tilt angle $\approx 14 \pm 18^\circ$). See ref 18 and 26.

(33) Our experimental protocol (see the Experimental Section) measured the ellipsometric constants of the substrate within 5 min of removal of the silicon wafer from the water in which it had been stored. Using the X-ray reflection technique, we have observed the slow (20–25 \AA in 24 h) buildup of a contaminating layer on a bare Si/SiO₂ substrate.

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(39) The substrates used in this study had a surface roughness on the order of 3–4 \AA . See ref 27.

(40) The simultaneous determination of the refractive index and length of the monolayer depends on the precision of the ellipsometric measurement. For the films studied here all refractive indices between 1.0 and 2.5 are possible for the index of the monolayer. See ref 29.

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(28) The inherent curvature of these thin substrates made it necessary, for the X-ray reflectivity measurements, to continually monitor the direction of the axis normal to the plane of the monolayer.

(29) McCrackin, F. L.; Passaglia, E.; Stromberg, R. R.; Steinberg, H. L. *J. Res. Natl. Bur. Stand., Sect. A* **1963**, *67*, 363–377.

(30) The refractive index of the Si/SiO₂ substrate varied slightly from sample to sample. The observed range of refractive indices was 3.84–3.89. The thicknesses of monolayers reported here were determined with the refractive index of the substrate on which that monolayer was prepared.

chosen to model the monolayer as a transparent medium with a refractive index of 1.45;⁴¹ other investigators have used a refractive index of 1.50 for organic monolayers.⁵ Our value is approximately that of pure liquid and crystalline paraffins (1.42–1.44)⁴² but is lower than that of high-density polyethylenes (1.49–1.55).⁴³ While our choice of refractive index is somewhat arbitrary, the X-ray reflectivity measurements (see below) suggest that the electron density in these monolayers is similar to that of bulk paraffins.^{44–47} For the monolayers examined here, an increase of 0.05 in the assumed value of the index of refraction of the monolayer would decrease its calculated thickness by ~ 0.8 – 1.3 Å.⁴⁸

For ellipsometry we used a helium–neon laser ($\lambda = 6328$ Å) as the light source. Other wavelengths within the visible region would provide similar results.⁵ The method has an accuracy on the order of ± 2 Å.

Low-Angle X-ray Reflectivity. The reflection of X-rays from surfaces⁶ has been used to characterize the structural properties of several systems, including liquids^{49–51} and liquid crystals.^{52–54} We and others have already described the theory of this technique⁵⁵ and its use for the characterization of the structure of monolayers prepared from alkyltrichlorosilanes.^{8,27} We will only summarize certain features of the method.

Low-angle X-ray reflectivity measures the intensity, R , of X-rays that are reflected from a surface as a function of the angle θ between the incoming X-ray beam and the sample. In general, the variation of this intensity with θ is given by Fresnel's laws. The intensity also varies as a result of the change in the difference in phase between X-rays reflected from the air–monolayer and monolayer–substrate interfaces. R is related to $\langle d\rho_{el}/dz \rangle$,⁵⁶ the average derivative of the electron density along the normal (z) axis of the substrate, by eq 4. Here hq_z (eq 5) is the change in

$$R = R_F |\rho_\infty|^{-1} \int_{-\infty}^{\infty} \langle d\rho_{el}/dz \rangle \exp(iq_z z) dz \quad (4)$$

$$q_z = 4\pi\lambda^{-1} \sin \theta \quad (5)$$

(41) A transparent medium does not absorb light and has a real refractive index.

(42) *CRC Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1975.

(43) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Ed.; John Wiley: New York, 1975; V-13–V-22.

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(46) The average electron density in these monolayers was ~ 0.30 Å⁻³. This value is slightly less than that of crystalline *n*-paraffins (0.32 Å⁻³). The latter value was calculated from the crystal structures of octadecane (C₁₈H₃₈) and eicosane (C₂₀H₄₂) given in ref 44 and 45.

(47) We can obtain an approximate value for the refractive index of the monolayer using the electron density of the monolayer, ρ_{el} , determined by the X-ray reflectivity measurements. This electron density can be converted to a mass density, ρ_m . An alternate form of eq 7 (see discussion on the projected area of alkylsiloxane groups) is given by eq i, where V is the volume of each

$$V = Ad = N_e/\rho_{el} \quad (i)$$

hydrocarbon tail in the monolayer. Since the mass of each tail, m , is simply the sum of the masses of each atom in the tail, the mass density of the monolayer can be calculated. The refractive index of a substance is related to its molar refractivity, R , mass density, and molecular weight, W , by eq ii.

$$(n^2 - 1)/(n^2 + 2) = R\rho_m/W \quad (ii)$$

R is found by summing the refractivities of each methylene and methyl group in the hydrocarbon tail (Vogel, A. I. *J. Chem. Soc.* **1948**, 1833–1855). This calculation yields an approximate refractive index of 1.50 ± 0.07 .

(48) The change in thickness of the monolayer as a function of its assumed refractive index is a linear function of the length of the monolayer: the longer the monolayer, the greater the change in the calculated thickness.

(49) Braslau, A.; Deutsch, M.; Pershan, P. S.; Weiss, A. H.; Als-Nielsen, J.; Bohr, J. *Phys. Rev. Lett.* **1985**, *54*, 114–117.

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(51) Sluis, D.; Rice, S. A. *J. Chem. Phys.* **1983**, *79*, 5658–5672.

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(56) ρ_{el} is the volume density of electrons: that is, the number of electrons present in a unit volume.

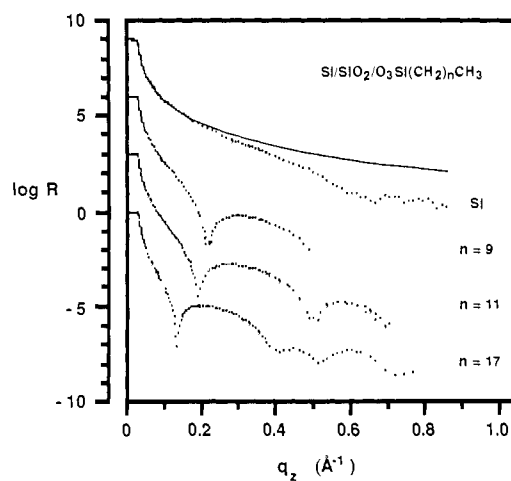


Figure 2. Intensity, R , of X-rays reflected from alkylsiloxane monolayers on silicon–silicon dioxide substrates as a function of q_z , the momentum change of the photon upon reflection. The monolayers were prepared from alkyltrichlorosilanes, $\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{CH}_3$. The top spectrum is for bare Si/SiO_2 . Each spectrum is offset by 10^3 from the one above it. The solid line is the calculated Fresnel reflectivity, R_F , for a perfectly smooth silicon substrate.

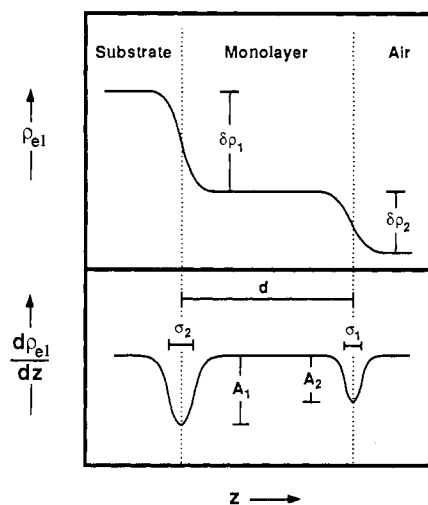


Figure 3. Models for ρ_{el} , the electron density, and $d\rho_{el}/dz$, the change in electron density along the normal perpendicular to the plane of the monolayer, used to analyze the measured X-ray reflectivity of alkylsiloxane monolayers on Si/SiO_2 substrates. The air–monolayer and monolayer–substrate interfaces are represented in $d\rho_{el}/dz$ by Gaussian functions, $A_1 \exp(z^2/2\sigma_1^2)$ and $A_2 \exp((z-d)^2/2\sigma_2^2)$. The parameter d , the separation between the air–monolayer and monolayer–substrate interfaces. This distance is the thickness of the monolayer. A_1 , A_2 , σ_1 , and σ_2 are the heights and widths of the Gaussian functions. The parameters $\delta\rho_1$ and $\delta\rho_2$ are the changes in refractive index across each interface and are proportional to $A_1\sigma_1$ and $A_2\sigma_2$. The electron density decreases from substrate to monolayer to air. The index of refraction for X-rays is a linear function of the electron density.

momentum experienced by the X-ray photons during the reflection process,⁵⁷ while ρ_∞ is the electron density of the bulk substrate. R_F is the Fresnel reflectivity, the intensity of X-rays reflected from a bare substrate whose boundary with a vacuum is sharp and perfectly smooth. If the refractive index of the substrate is known, the form of R_F is determined solely by the Fresnel reflection coefficients. This index of refraction is calculated from the critical angle, θ_c , for total reflection of the X-rays.⁵⁵ The refractive index in the X-ray region is a linear function of the electron density,

(57) The momentum, p , of a photon is $p = h/\lambda$. Since h is a constant, momentum can be represented by λ^{-1} , which has units of Å⁻¹.

ρ_{el} .⁵⁸ The change in electron density $d\rho_{el}/dz$ is therefore a direct measure of dn/dz .

Equation 4 describes the pattern of interference that results from the reflection of X-rays from an arbitrary electron distribution, $\rho_{el}(z)$. In the case of two sharp interfaces separated by some distance, eq 4 reduces to the familiar interference condition for reflection from parallel surfaces.^{59,60} Since the measured interference pattern depends on the actual distance separating the two interfaces in our monolayer system, this method, unlike ellipsometry, directly measures the thickness of the monolayer.

Our experiments utilized two monochromatized sources of X-rays: a rotating anode ($\lambda = 1.54 \text{ \AA}$) and the National Synchrotron Light Source (NSLS, $\lambda = 1.71 \text{ \AA}$). We present the data obtained from these two sources as a function of q_z because the interference pattern is invariant in q_z , regardless of the wavelength of radiation used. We will also usually present our data in the form R/R_F . Since for a single, sharp interface $R = R_F$,⁵⁹ $R/R_F = 1$ for all q_z . Any divergence of ρ_{el} from that characterizing a single, ideal interface is, therefore, readily apparent as deviations in R/R_F from a horizontal line.

The interpretation of the observed interference pattern (Figure 2 shows typical data) requires fitting it to a structural model of the monolayer that incorporates changes in the electron density along the surface normal ($d\rho_{el}/dz$). We have analyzed our data using a treatment described in detail elsewhere⁶¹ and summarized graphically in Figure 3. This two-layer model is the simplest plausible model for the description of the alkylsiloxane monolayers, but it is not an exact representation of the monolayer-substrate system. The presence of the surface oxide on the silicon substrate might suggest the use of a three-layer model. The electron densities of amorphous silicas and bulk silicon are, however, very similar.⁶² To the X-rays, the silicon and silicon dioxide therefore appear, to a first approximation, as a single material with no separating interface.⁶³ In this paper we will use the two-layer model to determine the thicknesses of the alkylsiloxane monolayers. In a separate paper²⁷ we discuss the uncertainties associated with this model and demonstrate how the thickness of the monolayer depends slightly on the model used.

Our model describes $d\rho_{el}/dz$ for each interface as a Gaussian function, $A \exp(z^2/2\sigma^2)$. The model contains five parameters: the thickness of the monolayer, d (actually the distance between the centers of the substrate-monolayer and monolayer-air interfaces), the height of each Gaussian, A_1 and A_2 , and their widths, σ_1 and σ_2 .⁶⁴ The σ parameters represent the roughnesses and intrinsic widths of both interfaces. The changes in electron density across each interface, $\delta\rho_1$ and $\delta\rho_2$, are proportional to $A_1\sigma_1$ and $A_2\sigma_2$, respectively. The positions of the minima in the X-ray profile are determined almost entirely by d . The thickness of the monolayer can therefore be determined to an accuracy of $\sim 1 \text{ \AA}$. The amplitudes of the minima, as well as the general shape of the profile of the scattered X-rays, reflect the combined effects of A_1 , A_2 , σ_1 , and σ_2 . Because these parameters are coupled, obtaining

(58) The index of refraction toward X-rays, n , is given by eq iii. This

$$n = 1 - (2\pi)^{-1} \lambda^2 \rho_{el} r_0 \quad r_0 = 2.818 \times 10^{-5} \text{ \AA} \quad (\text{iii})$$

relation is derived from the classical theory of dispersion for frequencies much higher than the resonance frequencies of the electrons in the sample. See ref 25, Chapter 2.

(59) See the appendix in the supplementary material.

(60) Halliday, D.; Resnick, R. *Physics*, 3rd ed., Part 2; John Wiley: New York, 1978; Section 45-5.

(61) Descriptions of this model and more sophisticated models for the structure of alkylsiloxane monolayers are found in ref 27.

(62) From the mass densities of silicon and quartz we calculate electron densities of 0.70 and 0.80 \AA^{-3} , respectively. Several mineral forms of silica, including opal and cristobalite, have densities 15% less than that of quartz. See ref 42.

(63) Inclusion of a third layer for the silicon dioxide on the substrate improves the overall agreement between the observed reflectivity and that predicted by the model, but it does not have a significant effect on the measured thickness of the monolayer. The presence of this layer in the model alters the calculated thickness by no more than 0.5 \AA . See ref 27.

(64) We refer to σ_1 and σ_2 as the roughnesses of the two interfaces in our model. They actually provide a measure of the distances over which the refractive index changes from n_0 (or n_1) to n_1 (or n_2).

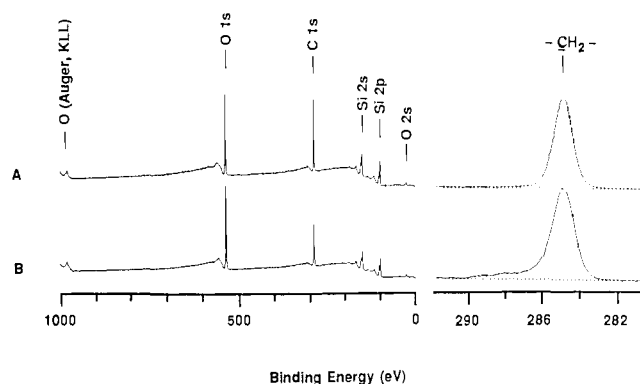


Figure 4. XPS spectra of a monolayer prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{CH}_3$ showing radiation damage caused by exposure to X-rays from a synchrotron source: survey spectra (left) and high resolution spectra of the C 1s region (right). A shows the edge of the sample that had not been exposed to X-rays. The contact angle in this region was $\theta_a^{\text{H}_2\text{O}} = 112^\circ$. The contact angle and XPS spectra of this area were indistinguishable from those of monolayers that had not been exposed to any X-ray radiation. No carbon atoms in oxidized environments are observed. B shows the central area of the sample that had been exposed to the greatest flux of X-rays. The contact angle in this region was $\theta_a^{\text{H}_2\text{O}} = 82^\circ$. The high-resolution C 1s spectrum exhibits a tail to higher binding energy, indicating the presence of oxidized carbon species.

reliable values for them is technically complex.²⁷

X-ray reflectivity does not utilize comparisons between the bare substrate and the coated sample to measure the thickness of the monolayer. Differences in susceptibility to contamination between the substrate and the monolayer would therefore have no effect on the measured length of the monolayer. Adsorption of impurities on the monolayer would, however, cause an increase in its apparent thickness. During the several hours required for the accumulation of the X-ray data, we have observed the buildup of a contaminant layer on the higher energy Si/SiO₂ surface.³³ We have not detected such contamination when a monolayer is present.

X-ray Damage. While ellipsometry is a nondestructive technique, exposure of an organic monolayer to synchrotron radiation results in some degradation of the sample. The experiments reported here were conducted under air rather than in vacuum or under an inert gas. We found that, upon removal from the X-ray beam, the contact angle of water on a methyl-terminated monolayer had decreased by $25\text{--}40^\circ$ from $\theta_a^{\text{H}_2\text{O}} = 112^\circ$ to $\theta_a^{\text{H}_2\text{O}} = 72\text{--}88^\circ$.⁶⁵ This lowered contact angle appeared only on the central portion of the sample: that is, the area that had been exposed to the greatest flux of X-rays. The edge of this sample, which had had little or no exposure to X-rays, exhibited unchanged wettability ($\theta_a^{\text{H}_2\text{O}} = 112^\circ$). Ellipsometry failed to discern any significant difference between the damaged and pristine regions.

Figure 4 represents XPS spectra of the C 1s peaks from the center and edge regions of a monolayer prepared from dodecyltrichlorosilane ($\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{CH}_3$). The damaged area, which had $\theta_a^{\text{H}_2\text{O}} = 82^\circ$, shows a tailing to higher binding energy that is not present in the areas unexposed to the radiation. We suspect that these changes in $\theta_a^{\text{H}_2\text{O}}$ and the XPS spectra reflect oxidation of the monolayer to polar, oxygen-containing functionalities (alcohols, ketones, carboxylic acids, hydroperoxides, and/or others).⁶⁶ We could not detect these new oxygen signals directly by XPS against the large background signal from the oxygen atoms in the surface silicon oxide. This type of damage apparently requires exposure to intense X-rays. Samples that had only been exposed to radiation from a rotating anode source, whose flux was approximately 0.1% of that of the synchrotron, exhibited no change in $\theta_a^{\text{H}_2\text{O}}$ or in XPS spectra.⁶⁷

(65) Two samples were analyzed under a helium atmosphere. Similar damage was observed for these samples as for those analyzed under air. The chamber holding the samples was not, however, air tight.

(66) The binding energies, relative to CH_2 , for oxidized carbon atoms are: CH_2OH , +1.5 eV; CO , +3.0 eV; CO_2H , +4.5 eV. Gelius, U.; Hedén, P. F.; Hedman, J.; Lindberg, B. J.; Manne, R.; Nordberg, R.; Nordling, C.; Siegbahn, K. *Phys. Scr.* **1970**, *2*, 70-80.

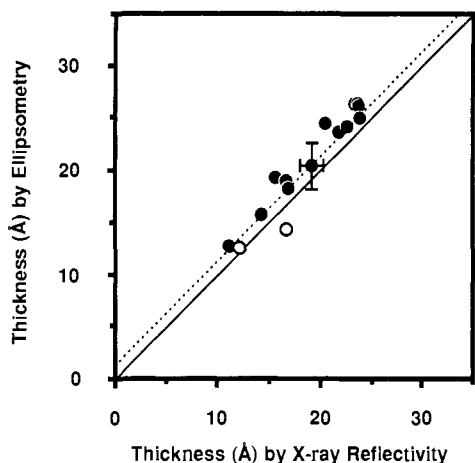


Figure 5. Comparison of the thicknesses of alkylsiloxane monolayers as measured by ellipsometry and X-ray reflectivity. The solid circles (●) are the thicknesses of complete monolayers; the open circles (○) are the thicknesses of partial monolayers. The solid line is that expected if the two techniques yield the same thickness. The dotted line is offset by 1.4 Å and is that expected if only ellipsometry includes the silicon atom of the alkylsilane in the measured thickness (see the text).

Although the damage to the monolayer was clearly measurable, we do not, for two reasons, believe that it had a significant effect on the value of the thickness measured for the monolayer. First, samples examined on both the rotating anode and the synchrotron exhibited similar reflectivities. Second, the information of primary importance in determining the thickness of the monolayer using the two-layer model—the position of the first intensity minimum in the reflected X-rays—was derived after relatively brief exposure to the X-rays.⁶⁸

Thickness of Alkylsiloxane Monolayers on Silicon. We applied both X-ray reflectivity and ellipsometry to a set of alkylsiloxane monolayers (Figure 5). For 15 samples and six chain lengths, the agreement between the two techniques is good. The maximum deviation between the thickness estimated using the two methods is 4.2 Å; the average difference is 2.2 Å (rms). This accuracy is equivalent to an error of $\sim 10\%$ in the measurement of the thickness of a C_{18} monolayer.

Ellipsometry systematically gives larger values of thickness. This difference could result from the use of too low a value for the refractive index of the monolayer. We would, however, require $n \approx 1.55$ in order to obtain values for the width of the monolayers from ellipsometry commensurate with those from the X-ray measurements. While such a high refractive index is found for crystalline polyethylene,⁴³ it seems unreasonable for a hydrocarbon monolayer that contains methyl groups.

We believe that the discrepancy between the thicknesses inferred from ellipsometric and X-ray measurements is, at least in part, the result of a subtle difference in the two methods. The ellipsometric thicknesses are based on differences in measurements of the bare substrate and the substrate with an attached alkylsiloxane monolayer. The refractive index of SiO_2 is 1.46⁶⁹ and the contribution of an O_3SiCH_2 moiety to the index of refraction of the monolayer is probably very close to that of the alkyl chain R. Thus, the thickness measured by ellipsometry includes the silicon atom of the alkylsiloxane group. In the X-ray experiment the measured thickness corresponds to the distance separating interfaces between media of different electron densities. Since the electron density of the silicon atom in the $RSiO_3$ group that attaches the monolayer to the substrate is effectively indistin-

(67) We were able to cause damage to these monolayers with a rotating anode by placing a monolayer in the direct beam of the anode for 24 h. The flux of this beam was $\sim 1/10$ that of the monochromatized radiation from the synchrotron. While the contact angle in the irradiated region decreased ($\theta_a^{H_2O} \approx 80^\circ$), XPS failed to find a significant surface concentration of oxidized carbon atoms.

(68) Sample deterioration will be important, however, in more detailed studies of how monolayer structure changes under various conditions.

(69) Taft, E. A. *J. Electrochem. Soc.* **1978**, *125*, 968–971.

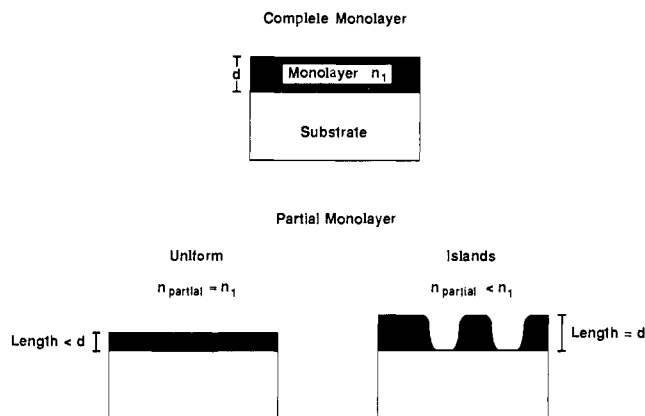


Figure 6. Models for the structure of incomplete monolayers. A complete monolayer has a thickness, d , and an index of refraction, n_1 . In the uniform model the partial monolayer has a length less than d and an index of refraction approximately equal to n_1 . In the island model the incomplete monolayer has a thickness, d , but the index of refraction is less than n_1 .

guishable from that of the oxide layer on the substrate, the silicon atom of the alkylsilane group appears to the X-rays to be part of the substrate, not of the hydrocarbon monolayer. In short, ellipsometry measures the thickness of a $Si(CH_2)_nCH_3$ monolayer; X-rays measure that of a $(CH_2)_nCH_3$ monolayer. This explanation suggests that thicknesses estimated by ellipsometry should be ~ 1.4 Å longer than those estimated by X-ray reflectivity.⁷⁰ These considerations cannot account for all the observed difference between the two sets of measurements. The remaining difference (~ 0.7 Å) probably reflects minor deficiencies in the models used in analyzing the ellipsometric and X-ray data.

Projected Area of Alkylsiloxane Groups in the Plane of the Monolayer. The data from low-angle X-ray scattering provides a semiquantitative estimate of the in-plane area of each alkylsiloxane group in these monolayers. The critical angle for total reflection from the substrate, θ_c , is related to the electron density of the silicon substrate ρ_{elSi} (eq 6).⁵⁵ The observed critical angle,

$$\theta_c^2 = \lambda^2 \rho_{el} r_0 / \pi \quad r_0 = 2.818 \times 10^{-5} \text{ \AA} \quad (6)$$

$\theta_c = 0.225 \pm 0.007^\circ$ for X-rays having wavelength $\lambda = 1.54 \text{ \AA}$,⁷¹ corresponds to an electron density of $0.72 \pm 0.05 \text{ \AA}^{-3}$. The expected value for silicon, 0.70 \AA^{-3} , is in good agreement with this number. The fitting of the profile of scattered X-rays to the model of $(d\rho_{el}/dz)$ for the covered substrate gives an estimate of the electron density of the monolayer, $\rho_{el,mono}$, relative to that of the substrate. For the n -alkane monolayers studied here, we estimate, using a three-layer model, that $\rho_{el,mono}/\rho_{elSi} = 0.43 \pm 0.05$.^{27,72} The area per alkylsiloxane group, A , can then be calculated from this estimate of the electron density of the monolayer, the thickness of the monolayer, d , and the number of electrons, N_e , in the alkyl group of each alkylsiloxane moiety (eq 7).⁷³ Our calculated value

$$A = N_e / d\rho_{el} \quad (7)$$

for A is $21 \pm 3 \text{ \AA}^2$ per RSi group.⁷⁴ An alternative analysis, based

(70) The size of the silicon atom is taken as half the sum of the projections of the Si–O (1.33 Å) and Si–C (1.52 Å) bonds onto the z axis. These projections were calculated from standard bond lengths assuming a bond angle of 109.5° .

(71) This value for the critical angle is slightly higher than the value $\theta_c = 0.221$ predicted by the electron density of crystalline silicon (0.70 \AA^{-3}). We attribute this discrepancy to curvature in the sample. See ref 27.

(72) The electron density of the monolayer, $0.30 \pm 0.03 \text{ \AA}^{-3}$, calculated with the theoretical critical angle for silicon (ref 71), corresponds to a mass density of $0.87 \pm 0.10 \text{ g/cm}^3$. This density is calculated assuming that the monolayer consists solely of methylene groups.

(73) The number of electrons in each constituent molecule of the monolayer was found by adding the number of electrons contributed by each atom in the tail of the silane, six for each carbon atom and one for each hydrogen.

(74) The major source of uncertainty in this estimate is the uncertainty in the electron density of the monolayer.

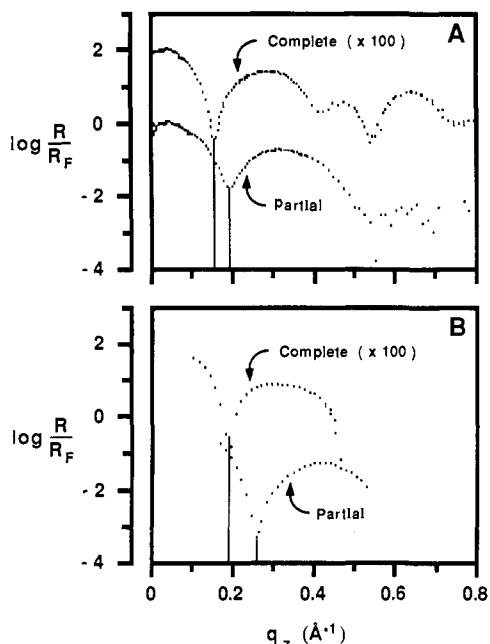


Figure 7. Comparison of the X-ray reflectivity, R/R_F , of partial and complete monolayers prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_n\text{CH}_3$: (A) $n = 17$ and (B) $n = 11$. The reflectivities of the complete monolayers are offset by a factor of 100.

on monolayers that had been prepared from dodecyl- and octadecyltrichlorosilane, yields an area of $22.5 \pm 2.5 \text{ \AA}^2$.²⁷ These areas are similar to that found for close-packed Langmuir-Blodgett monolayers of long-chain alcohols ($20.5\text{--}22 \text{ \AA}^2$)⁷⁵ and to the cross-sectional area per molecule within crystals of long-chain paraffins (20.5 \AA^2).^{44,45} Other studies have concluded that these self-assembled structures are themselves at or near a close-packed arrangement.¹⁸ Our results are consistent with this conclusion.

Structure of Incompletely Formed Monolayers. We would like to be able to assess the process by which alkyltrichlorosilanes adsorb and bind to a silicon substrate. While we cannot, with our current level of technical sophistication, directly analyze this process, we can determine certain features of the structure of incompletely formed (partial) monolayers. The analysis of these structures may, in turn, shed light on how complete monolayers are formed.

We generated partial monolayers by removing the substrates from the solutions containing the alkyltrichlorosilanes before the monolayers had formed completely. We hypothesized two extreme possibilities for the structure of such monolayers (Figure 6). A complete monolayer is characterized by a length, d , and a refractive index, n_1 . In one possible structure for an incomplete monolayer, the alkyl chains would be uniformly distributed over the substrate but would be disordered and have a liquidlike structure. In this "uniform" case, the monolayer would have a refractive index similar to that of the complete monolayer, but its thickness would be less. In the second structure, the monolayer would consist of islands of alkylsiloxane groups having local structure similar to that of the complete monolayer. In this "island" model, the thickness would be the same as that of the complete monolayer, but the average refractive index of the monolayer would be lower. We cannot, using ellipsometry, distinguish between these possibilities, since we must assume the refractive index of the monolayer in order to determine its thickness. X-ray reflection can, however, differentiate between these two models. For a structure containing islands, the positions of the minima in the X-ray profile would be the same as those of the complete monolayer since the distances between the air-monolayer and monolayer-substrate interfaces would be the same. The intensities of these minima would change because the average

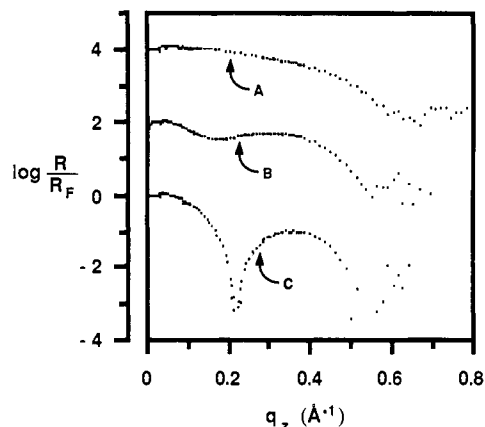


Figure 8. Effect of changing the electron density of the alkylsiloxane monolayer on the intensity of reflected X-rays, R/R_F : (A) Si/SiO₂ substrate, (B) monolayer prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$, and (C) monolayer prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_9\text{CH}_3$. A and B are offset by factors of 10^4 and 10^2 , respectively.

electron density within the island-containing structure would be lower than that within the complete monolayer. For the "uniform" structure the distance separating the interfaces would be less than that of the complete monolayer. Therefore, the locations of the minima would differ from those of the complete monolayer.

Figure 7 shows the intensity of X-rays reflected from two monolayers prepared from octadecyltrichlorosilane ($\text{Cl}_3\text{Si}(\text{CH}_2)_{17}\text{CH}_3$, OTS). The complete monolayer was prepared by immersing the silicon substrate in a solution containing OTS for 1 h. It had a thickness, by ellipsometry, of 26 \AA . The second sample was placed in the same solution for 40 s. By ellipsometry its thickness was 14 \AA , approximately 60% of that of the complete structure. There is an obvious shift in the position of the primary minimum for the complete and partial monolayers. This shift corresponds to a difference of 7 \AA in thickness, which is well beyond the experimental error of the experiment.

Figure 7 also presents similar data for two monolayers formed from dodecyltrichlorosilane ($\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{CH}_3$). While this set of data is not as complete as that for the monolayers prepared from OTS, the shift in the location of the minimum for the partial monolayer is also readily apparent. While in this latter system the incompleteness of the data set prevented us from obtaining reliable values for the electron density of the monolayer, the similarity in the amplitudes of the minima suggests that the electron density of the incomplete monolayer was similar to that of the complete structure.

We conclude that the structure of these partial monolayers is best described by the "uniform" model (Figure 6).⁷⁶ This conclusion differs from that of Sagiv,⁷⁷ which is based on an infrared study of partial ($\sim 60\%$) and complete monolayers prepared from OTS on aluminum by procedures similar to those used here.

Variation of the Electron Density of the Monolayer. The intensity of reflected X-rays at the interference minima in the X-ray profile is smallest when the intensities of light reflected from the substrate-monolayer and monolayer-air interfaces are equal. This condition is met when the electron density of the monolayer is approximately halfway between that of the silicon substrate and air. If the electron density of the organic layer is too close to that of the substrate or of air, the incoming X-rays see only one interface: that having a significant change in electron density.

We have demonstrated this effect by comparing the X-ray profiles for two monolayers formed from alkyltrichlorosilanes

(75) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966 and references cited therein.

(76) We do not generalize this result to other monolayer systems. The alkyltrichlorosilanes form a monolayer through the creation of covalent silicon-oxygen bonds between the silane and the substrate. Once bound to the substrate the molecules cannot move along the surface. For systems such as thiols on gold, where the monolayer is held on the substrate by weaker interactions, it may be possible for the monolayer constituents to diffuse laterally across the surface.

(77) Cohen, S. R.; Naaman, R.; Sagiv, J. *J. Phys. Chem.* **1986**, *90*, 3054-3056.

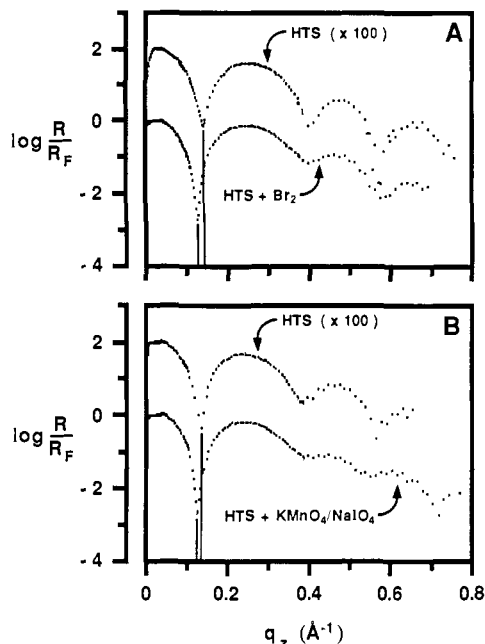


Figure 9. Change in the intensity of reflected X-rays that results from chemical transformations of vinyl-terminated alkylsiloxane monolayers prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$ (HTS): (A) addition of elemental bromine (2%, v/v, in CH_2Cl_2) to form CHBrCH_2Br or related brominated structures and (B) oxidation by KMnO_4 (0.5 mM)/ NaIO_4 (19.5 mM)/ K_2CO_3 (1.8 mM, pH 7.5) to CO_2H . For both A and B the upper X-ray profile, offset by a factor of 100, is that of the original monolayer; the lower is that after the transformation of the tail group of the monolayer.

containing 10 carbon atoms: $\text{Cl}_3\text{Si}(\text{CH}_2)_9\text{CH}_3$ and $\text{Cl}_3\text{Si}(\text{C}-\text{H}_2)_2(\text{CF}_2)_7\text{CF}_3$ (Figure 8). The fluorinated silane should generate a monolayer whose electron density is close to that of the silicon substrate. The amplitude of the minimum is much lower for the fluorinated alkylsiloxane than for the hydrocarbon. (The positions of the minima are different since the fluorinated silane has two electron density regimes along the normal axis, one for the layer containing the two CH_2 groups and one for the layer containing the eight-carbon perfluorinated chain. The alkylsiloxane monolayer containing the $(\text{CH}_2)_9\text{CH}_3$ group has a uniform electron density throughout the monolayer.)

Monolayers composed of hydrocarbon have electron densities midway between that of silicon and air and are very amenable to investigation by X-ray reflection. For other systems, such as the fluorinated monolayer on silicon shown in Figure 8 or hydrocarbon monolayers on transition metal substrates or on water, the acquisition of useful results from X-ray reflectivity will generally require detailed analysis.

Characterization of Chemical Reactions Involving a Monolayer.

We have begun to explore the use of X-ray reflectivity to study changes in the structures of monolayers when chemical reactions alter their composition. We had two interests in these studies. First, we wished to determine if X-ray reflectivity had the sensitivity to provide a new analytical technique with which to follow reactions involving monolayers. We were especially interested in its ability to detect small changes in electron density (for example that accompanying oxidation of a $\text{CH}=\text{CH}_2$ group to a CO_2H group). We were also concerned with its potential to damage the sample during analysis. Second, we wished to see if the structures of the alkylsiloxane monolayers were sufficiently rigid and well-ordered that we could incorporate into them layers having large values of $\langle d\rho_{\text{el}}/dz \rangle$ (for example, by adding Br_2 to a $\text{CH}=\text{CH}_2$ group to yield a CHBrCH_2Br moiety).

We have previously studied the addition of bromine to a monolayer prepared from $\text{Cl}_3\text{Si}(\text{CH}_2)_{15}\text{CH}=\text{CH}_2$ (HTS).¹⁶ The contact angle of water on this vinyl-terminated monolayer was $\theta_{\text{H}_2\text{O}}^{\text{H}_2\text{O}} = 100^\circ$. Reaction with elemental bromine generated what we hypothesized to be the corresponding 1,2-dibromide (and other related brominated species)⁷⁸ and resulted in a decrease in $\theta_{\text{H}_2\text{O}}^{\text{H}_2\text{O}}$

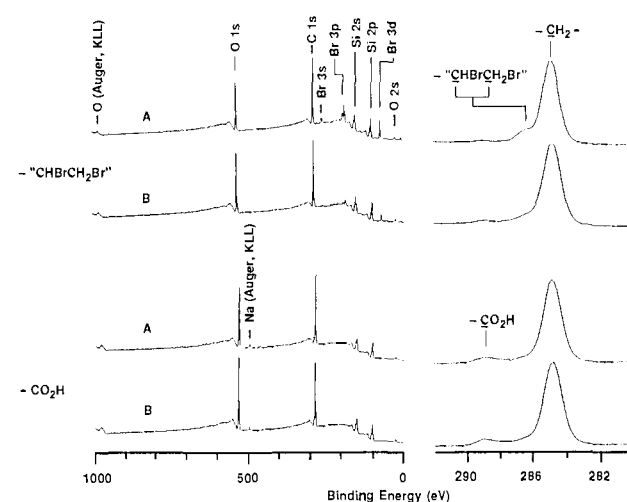


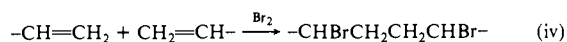
Figure 10. XPS spectra of alkylsiloxane monolayers terminated with CHBrCH_2Br (and related brominated species, indicated by “ CHBrCH_2Br ”) and CO_2H groups after exposure to X-ray radiation from a synchrotron source: survey spectra (left) and high-resolution spectra of the C 1s region (right): (A) edge of monolayer that had not been exposed to any synchrotron X-ray radiation and (B) central area that had been irradiated with the greatest flux of X-rays.

to $\sim 80^\circ$. XPS spectra confirmed the incorporation of bromine into the monolayer. Ellipsometry suggested that the monolayer had lengthened by 2–3 Å.⁷⁹

Figure 9 presents X-ray reflectivity data for the bromination of a monolayer prepared from HTS. Reflectivities were measured from a single monolayer before and after exposure to a solution of elemental bromine in CH_2Cl_2 . After reaction, the primary minimum shifted to lower q_z ($\Delta q_z = 0.014 \text{ \AA}^{-1}$). Since the bromination effectively lengthens the monolayer by one atomic center,⁸⁰ this change is expected and is consistent with the ellipsometric data. The addition of one methylene unit to a saturated alkyl chain containing 17 carbon atoms would shift q_z by 0.0063 \AA^{-1} .⁸¹ The intensities of the minima also changed upon bromination; the primary minimum deepened while the second decreased in amplitude.

If the bromine were localized in the position of the double bond in a trans-extended conformation for the organic chain, we would expect to infer from the X-ray reflectivity a layer approximately 4-Å thick with an electron density several times that of the hydrocarbon. Fitting the intensity data to a three-layer model did

(78) Because of the high density of vinyl groups at the air–monolayer interface, bromination of these groups could conceivably induce some polymerization of the type presented in eq iv.



(79) In using ellipsometry to follow reactions, we continued to use a refractive index of 1.45. This approach is clearly arbitrary, but we have found that even using the refractive index of elemental bromine (1.66) to describe the new layer on the surface alters our estimate of the change in thickness by only $\sim 0.4 \text{ \AA}$.

(80) The van der Waals radius of bromine (1.95 Å) is slightly less than the sum of the covalent radii of carbon (0.77 Å) and hydrogen (0.37 Å) and the van der Waals radius of hydrogen (1.2 Å). The volume occupied by a bromine atom is therefore similar to that of a methyl group. *Lange's Handbook of Chemistry*, 11th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1973.

(81) We have calculated the expected change in q_z using the assumption that the monolayer–air and monolayer–substrate interfaces are perfectly sharp. In the appendix (see the supplementary material) we show that this assumption yields the usual condition for destructive interference (eq J). For the primary minimum in R , n in equations H, I, and J is zero. Rearrangement of equation H with $n = 0$ results in equation v for the location of the primary

$$q_{z0} = \pi/d \quad (\text{v})$$

minimum, q_{z0} , as a function of d , the distance between the two interfaces. Values for d were calculated using standard bond lengths and a bond angle of 109.5° .

find a localized layer of high electron density. The best fit to the data, however, suggested a rather broad layer (6 Å (fwhm) in thickness) whose electron density corresponded to approximately 60% of that expected for complete bromination of the vinyl groups in the monolayer.

These results do not indicate a well-ordered, layered structure for the brominated monolayer derived from HTS.⁸² Their interpretation is, however, complicated by X-ray damage to the brominated sample during the reflection measurements, by uncertainty concerning the structures formed on bromination, and by damage to the sample during the reflectivity measurements before reaction with bromine. After measurement of the X-ray reflectivity of the vinyl-terminated monolayer prior to bromination, the central region of the sample had a contact angle with water approximately 30° lower than the edges of the sample that were outside of the X-ray beam. After bromination, the central area of this sample had a contact angle of $\theta_a^{\text{H}_2\text{O}} = 67^\circ$, 11° less than that of the edge ($\theta_a^{\text{H}_2\text{O}} = 78^\circ$). Figure 10 presents XPS spectra for the brominated monolayer. The survey spectra indicate that there was only one-third as much bromine in the region exposed to the X-rays as in the section not exposed to the radiation. The C 1s spectra were also qualitatively different in these regions: the exposed area showed several different carbon environments with binding energies at least 3 eV higher than that of CH₂. Since the contact angles on the surface of the vinyl-terminated monolayer indicated some degree of radiation damage prior to the bromination of the monolayer, the reduced concentration of bromine that we observed probably reflects a combination of two effects: first, the radiation destroyed some fraction of the initial vinyl groups, and second, the synchrotron radiation removed some of the bromine that had added to the remaining vinyl groups.^{83,84}

Figure 9 presents analogous reflectivity data for materials obtained by oxidation with KMnO₄ and NaIO₄ of monolayers prepared from HTS. The expected product of this reaction is a carboxylic acid.⁸⁵ As for the bromination, we measured the reflectivity from a single monolayer before and after reaction. The X-ray data indicated a slight increase in the thickness of the monolayer on oxidation, although this change in thickness was not as large ($\Delta q_z = 0.008 \text{ \AA}^{-1}$) as that observed on bromination. The second minimum was also reduced in amplitude after the oxidation. Since this reaction replaces a carbon atom with two oxygen atoms, but does not add to the end-to-end length of the chain, we do not expect the change in the thickness of the monolayer to be as large in this reaction as in the bromination reaction. Attempts to model the observed data suggested that there was a high-density region at the air-monolayer interface. The agreement between the model and the data was, however, poor.

Contact-angle measurements on the vinyl-terminated monolayer after the determination of its X-ray reflectivity revealed typical radiation damage. After the reflectivity measurements on the oxidized monolayer there was, however, no observable difference in the contact angles of water ($\theta_a^{\text{H}_2\text{O}} \approx 40^\circ$) between the region of the sample which had been exposed to X-rays and the regions which had not. The XPS spectra (Figure 10) also show no difference between the irradiated and unirradiated regions. This apparent uniformity in the surface and the resulting implication that X-ray damage is not important in these X-ray reflectivity experiments is reasonable but possibly misleading. Both the KMnO₄/NaIO₄ oxidation and the synchrotron radiation would be expected to generate oxidized species in the monolayer, and it might not be possible for us to detect radiation damage in this oxidized system.

(82) While angle-resolved XPS studies might shed some light on the distribution of bromine within the monolayer, we have had difficulty obtaining reproducible results from brominated monolayers which had not been exposed to synchrotron radiation. See ref 16.

(83) We have observed a decrease in the intensity of the bromine signal during the accumulation of the XPS spectra. While the flux of X-rays in the spectrometer is unknown, it is certainly less than that of the X-ray beam from the synchrotron.

(84) The binding energy of the bromine in the damaged region (Br 3d_{5/2}, 70.5 eV) was identical with that in the areas unexposed to the X-rays.

(85) Lemieux, R. U.; von Rudloff, E. *Can. J. Chem.* **1955**, *33*, 1701-1709.

Discussion

This work makes it possible to compare measurements of the thickness of alkylsiloxane monolayers on silicon using two techniques: optical ellipsometry and low-angle X-ray reflectivity. The former technique is more convenient than the latter, but its use requires certain assumptions whose correctness is difficult to check. The good agreement between results from these independent techniques strongly supports the accuracy of the thicknesses from ellipsometry. The small, systematic differences observed between these sets of results emphasizes the importance of detailed consideration of the structure and properties of the interfaces involved in reflecting light in the optical and X-ray regions of the spectrum.

Ultimately the correctness of ellipsometry relies on the proper choice for the refractive index of the monolayer. While the agreement between the X-ray and ellipsometric results is not sufficient to determine this index accurately, we note that the electron density of the monolayer is apparently independent of both the degree of completeness of the monolayer and the length of the alkyl group in the silane. Using the same refractive index for all samples, whether partial or fully formed, therefore appears justified. This conclusion differs from that reached for partial, "skeletalized" films prepared by the etching of Langmuir-Blodgett multilayers, rather than the direct deposition of partially formed monolayers.^{86,87} It is plausible that this type of manipulation might yield an island structure rather than the apparently uniform partial monolayers studied here.

The information available from X-ray reflectivity concerning organic monolayer films is complementary to that available from other techniques. X-ray reflectivity requires no a priori assumptions about the structure (index of refraction, roughness, thickness) of the sample. It has a sensitivity to atomic-scale structure that comes with the short wavelength of X-ray light. In addition, the ability of X-rays to penetrate solids makes it applicable to buried interfaces, even if the overlying film is not transparent in the optical spectrum.

X-ray reflectivity also has several limitations. First, it requires a suitably flat substrate. At present, highly polished glass, float glass, and silicon are the only solids that have been shown to have satisfactory flatness,^{88,89} although a number of liquids⁴⁹⁻⁵¹ and liquid crystals⁵²⁻⁵⁴ have been examined with this technique. Recent progress in the epitaxial growth of metal surfaces⁹⁰ and the preparation of ultrasurface⁹¹ suggests that the extension of this technique to other substrates will soon be possible. Second, the electron density of the monolayer must be different from that of both the substrate and air; too close matching with either results in an ill-defined interface (that is, a small value of $\langle d\rho_{\text{el}}/dz \rangle$ at the interface) and a decrease in sensitivity and resolution. Third, organic samples may be damaged by exposure to high-intensity X-rays. Irradiation of these monolayers in the presence of dioxygen appeared to result in oxidation. Exposure of monolayers containing C-Br bonds results in a loss of bromine. This type of loss is also observed during XPS analysis under conditions that do not damage methyl- or vinyl-terminated monolayers.¹⁶ How important these damage processes are in causing artifacts in the data and how effectively they can be suppressed by changing experimental conditions (for example, by using inert atmospheres or vacuum, low temperatures, or short exposure times) remains to be established. We believe that better control over the conditions under which X-ray reflectivity measurements are made will permit the use of this technique for the detailed analysis of the structure of monolayer systems.

Experimental Section

Materials. Decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecyl-trichlorosilane were obtained from Petrarch Systems and distilled prior

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to use. The compound 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyltrichlorosilane ($\text{C}_{12}\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$) was obtained from Petrarch and used as received. The synthesis of 16-heptadecenytrichlorosilane (HTS) has been described previously.¹⁵ Hexadecane and bicyclohexyl were obtained from Aldrich and purified by percolating twice through neutral, grade 1, activated (as purchased) alumina (Fisher). The purified solvents passed the Bigelow test for polar impurities.⁹² Silicon (100) was obtained in 3-in. diameter wafers from Semiconductor Processing Corp (Boston, MA) (n-type, laser grade) in three thicknesses, 0.080, 0.125, and 0.200 in., and from Monsanto (p-type, 0.015 in.). Water was passed through an ion exchanger (Cole-Parmer) and distilled in a Corning Model AG-1b glass distillation apparatus.

Preparation of Monolayers. The silicon wafers were cut into strips 1-in. wide. These strips were cleaned by heating in a solution of concentrated H_2SO_4 and 30% H_2O_2 (70:30 v/v) at 90 °C for 30 min.⁹³ (CAUTION: "piranha" solution reacts violently with many organic materials and should be handled with great care.) The substrates were rinsed thoroughly with distilled water and stored under water until use.

The cleaned silicon strips were removed from water using Teflon-coated forceps (Pelco). All visible traces of water were eliminated by exposing the sample to a stream of argon (minimum purity 99.995%) for ~30 s. The silicon was then placed in a ~0.5% w/w solution of the alkyltrichlorosilane in hexadecane or bicyclohexyl. The containers for the solution were custom-made from rectangular glass tubing that had one end sealed. Prior to use and during the formation of the alkylsiloxane monolayers, the containers were kept either under a dry nitrogen atmosphere or in a desiccator containing P_2O_5 (Baker, "granulic"). After 1 h (desiccator) or 24 h (nitrogen atmosphere), the substrate was removed from solution and placed in 100 mL of CHCl_3 for 15 min to remove any microscopic contaminants that might have adsorbed onto the surface of the monolayer. The sample was then immersed in 100 mL of ethanol for 30 s and rinsed with ethanol dispensed from a 2-mL disposable pipet. The monolayer was dried under a stream of argon and measurements of contact angle and ellipsometry were made immediately.

Contact Angles. Advancing contact angles were determined on sessile drops with a Ramé-Hart Model 100 contact angle goniometer equipped with a controlled-environment chamber. The relative humidity in the chamber was maintained at >80% by filling the wells of the sample chamber with water. The temperature was not controlled and varied from 20 to 25 °C. The volume of the drop used was 3 μL ; its pH was ~5.6. All reported values are the average of at least four measurements on the film surface and have a maximum range of $\pm 3^\circ$.

Ellipsometry. Ellipsometric measurements were made with a Rudolph Research Model 43603-200E thin-film ellipsometer. The light source was a He-Ne laser ($\lambda = 6328 \text{ \AA}$). The angle of incidence was 70.0° (relative to the normal of the plane of the sample) and the compensator was set at -45.0°. The measurements necessary for the calculation of the film thickness consisted of the determination of the polarizer and analyzer angles for the silicon substrate and the corresponding set of angles for the substrate coated with a monolayer film.

Each set of analyzer and polarizer readings, measured in zones 1 and 3,⁹⁴ were the average of at least four measurements taken at different locations (separated by at least 1 cm) on the sample. The angles that comprised this average had a maximum scatter of $\pm 0.15^\circ$. These measurements were determined in air for the bare substrate within 5 min of its removal from water. The substrate was placed in the solution of alkyltrichlorosilane immediately after these measurements. Measurements for the substrate-monolayer systems were taken no more than 5 min after the samples had been washed with ethanol.

The refractive index of the substrate was calculated from the analyzer and polarizer angles for the uncoated silicon. This value was then used to determine the thickness of the monolayer according to the algorithm of McCrackin.²⁹ The lengths were calculated assuming that the monolayer had a refractive index of 1.45. The algorithm calculated two values for the length of the monolayer, both of which were complex. Since the length of the monolayer must be real, we chose the real part of the complex number with the smaller imaginary component as the thickness of the monolayer. (The other choice was inherently unreasonable since it was greater than 1000 Å .) Thicknesses determined in this way are accurate to $\pm 2 \text{ \AA}$.

X-ray Photoelectron Spectroscopy. The XPS spectra were obtained using a Surface Science Laboratories Model SSX-100 spectrometer (monochromatized Al $K\alpha$ X-ray source; 10^{-8} – 10^{-9} Torr) referenced to Au 4f_{7/2} at 84.0 eV. Samples were washed with ethanol, dried under a

stream of argon, and introduced into the spectrometer. For each sample a survey spectrum (resolution 1.1 eV, spot size 1000 μm , one scan) and high-resolution spectra of the peaks for C 1s, O 1s, Br 3d, and Si 2p (resolution 0.16 eV, spot size 300 μm , 10–30 scans) were collected. Atomic compositions were determined with standard multiplex fitting routines and the following sensitivity factors: C 1s, 1.00; O 1s, 2.49; Si 2p, 0.90; Br 3d, 3.188.⁹⁵

X-ray Reflection Measurements. X-ray sources were a Rigaku rotating-anode (RA) X-ray generator (Cu $K\alpha_1$ radiation, $\lambda = 1.54 \text{ \AA}$, 90 mA, 45 keV) and the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (beam line X-22B, $\lambda = 1.71 \text{ \AA}$). Monochromatic radiation was obtained by reflection from a monochromator (RA, triple-bounce germanium (111); NSLS, single-bounce germanium (111)). The beam size was $0.1 \times 5 \text{ mm}$ for incident angles less than 1° and $0.5 \times 5 \text{ mm}$ for incident angles greater than 1° . X-rays were monitored with two scintillation detectors: one for the incoming beam, the other for the radiation reflected from the sample. The intensities of the reflected X-rays were normalized to the intensity of the incoming beam.

Since the background radiation was a function of the angle of the incoming beam, point by point background subtraction was performed. The background was determined by purposely misaligning the detector by $\pm 0.3^\circ$ at each incident angle θ .

Samples were mounted in a brass cell with Kapton (Du Pont) windows. The chamber excluded X-rays at angles greater than 7° . The atmosphere in the chamber was either air or helium.

The range of intensities that could be detected was 10^6 with the rotating anode and 10^9 at NSLS. A typical reflection scan required 15 h on the rotating anode and 4 h at NSLS. The data that was obtained at NSLS covered twice the range in q_z as that from the rotating anode.

Bromination. The X-ray reflectivity for a monolayer prepared from HTS was measured as above. This monolayer was then placed in a 2% (by volume) solution of elemental bromine in CH_2Cl_2 for 7 h. The wafer was then rinsed in CH_2Cl_2 and in ethanol. The reflectivity was then measured again.

Oxidation. As for the bromination, the reflectivities before and after oxidation were measured as described above. Stock solutions of KMnO_4 (5 mM), NaIO_4 (195 mM), and K_2CO_3 (18 mM) in water were prepared. Immediately prior to the oxidation, 10 mL of each of these solutions was combined with 70 mL of distilled water to create the oxidizing solution (KMnO_4 , 0.5 mM; NaIO_4 , 19.5 mM; K_2CO_3 , 1.8 mM, pH 7.5). The monolayer prepared from HTS was placed in this solution for 2 h at 75 °C. The sample was removed from the oxidant and rinsed in 100 mL of each of NaHSO_3 (0.3 M), water, 0.1 N HCl, water, and ethanol.

Pentadecyltrichlorosilane. Dihydrogen hexachloroplatinate(II) (Alfa, 5.3 mL of a 0.01 M solution in THF, 0.053 mmol), trichlorosilane (Petrarch, 8.6 mL, 85 mmol), and 1-pentadecene (Aldrich, 15.01 g, 71 mmol) were placed under argon in a dry, heavy-walled glass tube (diameter 2.5 cm, length 21 cm) equipped with a sidearm and a 0–10 mm PTFE stopcock. The solution was degassed (freeze-pump-thaw, three cycles) and the tube was sealed under vacuum at -195 °C. The tube was then warmed to room temperature, after which it was heated in an oil bath (99 °C, 43 h). The tube was then cooled to room temperature. The reaction solution was transferred to a 100-mL round-bottomed flask equipped with a vacuum adapter. A liquid nitrogen cooled trap was attached and the excess trichlorosilane and THF were removed by a trap-to-trap distillation. The remaining liquid was distilled in a dry Kugelrohr distillation apparatus. The product (15.3 g, 44 mmol, 62%) was the fraction collected from 95 °C (0.013 Torr) to 105 °C (0.010 Torr).

¹H NMR (CDCl_3): δ 1.7–1.2 (m, 28), 0.9 (t, 3). ¹³C NMR (CDCl_3): δ 32.24, 32.01, 30.00, 29.94, 29.89, 29.68, 29.25, 24.50, 22.98, 22.51, 14.29. Anal. Calcd for $\text{C}_{15}\text{H}_{31}\text{Cl}_3\text{Si}$: C, 52.08; H, 9.05; Cl, 30.75. Found: C, 51.89; H, 9.12; Cl, 30.95.

Acknowledgment. This research was supported by the Office of Naval Research, the Defense Advanced Research Projects Agency (through the University Research Initiative), the National Science Foundation (Grant DMR 86-14003 to the Harvard Materials Research Laboratory), and the Joint Services Electronics Program of the Department of Defense (Grant N0014-84-K-0465). XPS spectra were obtained with instrumental facilities purchased under the DARPA/URI program and maintained by

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the Harvard University MRL. The rotating-anode facility is part of the MRL. The synchrotron measurements were carried out at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Research at the NSLS is supported by the Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC02-76CH00016. Ian Tidswell was the recipient of a NATO studentship. We are grateful to Dr. David Osterman and Dr. Thomas Rabedeau for assistance in these experiments, to Dr. Abraham Ulman of Eastman Kodak for providing preprints of articles, and to Dr. Ralph Nuzzo of AT&T

Bell Laboratories for helpful discussions.

Registry No. HTS, 120905-09-1; Si, 7440-21-3; $\text{Cl}_3\text{Si}(\text{CH}_2)_{14}\text{CH}_3$, 60592-74-7; $\text{Cl}_3\text{Si}(\text{CH}_2)_9\text{CH}_3$, 13829-21-5; $\text{Cl}_3\text{Si}(\text{CH}_2)_{11}\text{CH}_3$, 4484-72-4; $\text{Cl}_3\text{Si}(\text{CH}_2)_{13}\text{CH}_3$, 18402-22-7; $\text{Cl}_3\text{Si}(\text{CH}_2)_{15}\text{CH}_3$, 5894-60-0; $\text{Cl}_3\text{Si}(\text{C}-\text{H}_2)_{17}\text{CH}_3$, 112-04-9; $\text{Cl}_3\text{Si}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3$, 78560-44-8.

Supplementary Material Available: An appendix outlining the intensity of reflected X-rays for certain electron-density profiles (4 pages). Ordering information is given on any current masthead page.

Kinetic (Not Equilibrium) Factors Are Dominant in Wittig Reactions of Conjugated Ylides

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Abstract: The Wittig reaction of ester-, vinyl-, or benzyl-stabilized ylides is examined in detail. Extensive control experiments have been performed to probe the oxaphosphetane intermediates, and reversal in these systems is ruled out as a significant (>5%) process. Betaine reversal, on the other hand, can be detected in the control experiments, depending on the conditions. Maximum betaine reversal is associated with formation of the anti betaine rotamers, while syn betaines can be generated in ethanol or THF without significant reversal in several cases. It is emphasized that betaines are obligatory intermediates in the control experiments, but they are neither obligatory nor likely intermediates in Wittig reactions, especially the *E*-selective examples conducted in aprotic solvents. Only the oxaphosphetanes are required to describe the overall Wittig process from ylide to alkene. Other intermediates are not necessary, including zwitterions, specific conformers, pseudorotamers, etc. The traditional control experiments are more complex and are shown to involve anti betaines as well as syn betaines (**2**, **24**, **25**), and in certain cases, hydroxy ylides (**28**) derived from the betaines. The *E*-selective reactions of ester-stabilized ylides are described as asynchronous cycloadditions with a relatively advanced, oxaphosphetane-like transition state. Exceptionally *E*-selective olefination is achieved using the allylic dibenzophosphole ylide **11a**. The intermediate oxaphosphetanes **14a**, **15a**, and **15b** are observed for the first time in a conjugated-ylide reaction.

The stereochemistry of the Wittig reaction is influenced by the presence of π -acceptor groups at the α -carbon.^{1,2} Ylides $\text{Ph}_3\text{P}=\text{CHX}$ or $\text{Ph}_2\text{RP}=\text{CHX}$ (X = ester, acyl, vinyl, aryl, etc.) generally react with high (*E*)-olefin selectivity compared to the "nonstabilized" ylides $\text{Ph}_3\text{P}=\text{CHCH}_3$ or $\text{Ph}_2\text{RP}=\text{CHCH}_3$. House et al. reported increased (*Z*)-olefin formation from $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ in methanol vs aprotic solvents and considered possible explanations based on the interconversion of betaine diastereomers **2a** and **3a** (eq 1).^{2b} Although House did not choose among the mechanistic alternatives due to insufficient kinetic data, the connection between betaine interconversion and *E* selectivity became widely accepted in the review literature.¹ Some years later, extensive studies of solvent effects were interpreted to favor a cycloaddition mechanism for carbonyl-stabilized ylides.³ Shortly thereafter, it was shown that oxaphosphetanes, not betaines, are observed in Wittig reactions where an intermediate can be detected.^{4a} Subsequent proposals for interconversion of diastereomeric intermediates have discussed pathways that do not de-

pend on betaines.⁵ However, there is limited experimental evidence regarding the extent of equilibration by any means in conjugated ylide reactions.

Two important studies have appeared that support the idea that betaines can equilibrate. Speziale and Bissing found that treatment of ethyl *trans*-phenylglycidate with triphenylphosphine (refluxing ethanol) in the presence of *m*- $\text{ClC}_6\text{H}_4\text{CHO}$ affords crossover products corresponding to the reversal of an intermediate betaine **2a** (eq 2).⁶ Analogous results were obtained with stilbene oxide and other epoxides under more drastic conditions.^{6,7} Trippett and Jones demonstrated that a betaine, **2b**, generated by deprotonation of the β -hydroxy phosphonium salt **6b** with NaOEt/EtOH, also affords extensive crossover products with $\text{ClC}_6\text{H}_4\text{CHO}$ (Scheme I).⁸ All of the essential features of these studies have been confirmed in our laboratory. However, when the betaine **2b** is formed by the quaternization of a phosphine alkoxide, **7b**, with methyl iodide in THF, (*Z*)-stilbene is obtained with 98% retention.⁹ Furthermore, when **2c** is generated by the deprotonation method from **6c** in methanol, (*Z*)-cinnamate is formed in high yield.¹⁰ These observations imply that equilibration of

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