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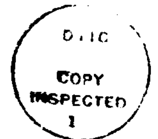

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ATTENUATED TOTAL REFLECTION FTIR SPECTROSCOPY FOR MEASURING INTERFACIAL REACTION KINETICS AT SILICA SURFACES

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Abstract Attenuated total reflection (ATR) FTIR spectroscopy has been adapted to measure the rates of chemical reactions which modify silica surfaces. In this method, a silicon ATR substrate is oxidized to produce a silicon dioxide surface layer, which can be used as a model silica surface in measurements of the rates chemical modification. An ATR flow cell is filled with a solution of a surface active reagent, and spectra are obtained at regular intervals. Confinement of the infrared intensity to the interface by total internal reflection provides a measure of changes in concentrations of species which adsorb or bind to the surface.

INTRODUCTION

Understanding the chemical modification of silica and glass surfaces continues to be a challenging area of surface science. The results of such investigations can impact many areas of technology, including adhesion and composite materials, chemical separations using modified silica surfaces, chemical passivation of oxide surfaces, and immobilization of chemical reagents on silica and glass. Structural and kinetic information about this chemistry can advance the understanding and development of these systems.

Spectroscopic methods have been applied to study adsorbates at gas-solid interfaces, using differential infrared spectroscopy.[1,2] Studies of molecular adsorption and chemical bonding from the liquid state onto solid surfaces have generally been limited to examination of the surface before and after exposure to determine what compounds are retained.[3,4] Such studies have left to speculation the rates of reaction and the surface interactions responsible for the observed results. The ability to follow, in situ, the kinetics of bonding of a species at a liquid/solid interface using infrared spectroscopy is a useful goal for acquiring information about interfacial reaction mechanisms and factors which affect the rates of reaction.

A variety of infrared techniques have been applied to studying

molecules adsorbed and bound to silica and glass surfaces. The high surface areas of microparticulate silica[6] and glass fibers[7] yield large concentrations of surface species which allow measurement by standard infrared techniques. Spectroscopic data in these studies were gathered following exposure of silica or glass fiber substrates to a reagent or adsorbate, rinsing and drying the substrate, and collecting spectra against a gas or vacuum interface. Attenuated total reflection (ATR) FTIR can be employed to measure monolayer infrared spectra at optically flat surfaces in the presence of solvent.[5] Despite the lower sensitivity due to the smaller surface area, optically flat substrates measured with ATR methods offer an important advantage of controlling the depth of penetration of the radiation beyond the interface. ATR-FTIR measurements of the formation of monolayers of polyfunctional silane reagents on elemental silicon substrates have been carried out.[8] Again, this study involved removing the substrate from solution and collecting spectra _ex situ_, after reaction had occurred. The ATR technique has also been used for studying _in situ_ adsorption rates. The earliest example of _in situ_ ATR-IR kinetics was the measurement of stearic acid adsorption from CCl_4 solution on Germanium, using both dispersive and Fourier transform techniques.[9] Recently, the total internal reflection method has been applied to more complex liquid/solid interface problems including observation of the adsorption of biopolymers[10] and polymethylmethacrylate[11] on commercially available ATR substrates.

Based on these ATR-FTIR developments, an opportunity exists for applying this method to real-time monitoring of the surface reaction kinetics and for following the reagent-surface interactions during the course of such reactions. To understand the reactions of silane reagents with silica, glass, or other oxide surfaces, one must carry out such reactions at an appropriate model oxide interface. In this paper, we describe the use of a polycrystalline silicon ATR substrate, surface modified by a controlled oxidation, so that the substrate is coated with a well-controlled silicon dioxide layer. Methods for growing silicon dioxide films on silicon wafers are widely available. The defect structures,[12] hydride and hydroxyl concentrations,[13] and interface roughness[14] for such films have been characterized.

The silicon dioxide layer provides a suitable model interface for studying chemical modification of silica or glass, while the infrared transparency of the silicon substrate allows ATR-FTIR measurements for monitoring the course of the reaction. This method has been evaluated in a study of the reaction of a monofunctional silane reagent, diphenylchlorosilane (DPCS), with the silica surface in carbon tetrachloride.[15] The method has also been used in a study of the silica reaction with two related trifunctional silanes of biomaterials interest, 3-mercaptopropyltrimethoxy silane (MPS), and dithiopyridine protected MPS (PDS-MPS) in cyclohexane;[16] these latter silanes represent potential surface linkages with proteins via the formation of a disulfide bond. Since the rates of reaction of these reagents with the surface are relatively slow, many ATR-FTIR difference spectra can be gathered over the course of the reaction providing kinetic as well as structural data.

EXPERIMENTAL METHODS

ATR-FTIR Kinetic Measurements

Preparation of the silica surface on an ATR silicon substrate by controlled oxidation has been previously described.[15] The flow cell containing the oxidized substrate was placed and aligned in the dry air or CO_2-purged sample compartment of the spectrophotometer, and a background spectrum was collected. A second background spectrum was collected once the cell was filled with the solution containing the silane reagent. Control of the instrument was then passed to a program which collected a difference spectrum every 5-7 minutes, using the second background spectrum above as a reference. After the experiment ran for 2 hours, a final difference spectrum was collected, using the first background spectrum as a reference. The crystal was then removed from the holder and rinsed with cyclohexane and allowed to dry. Ellipsometry data on the crystal were again collected after each surface derivatization and analyzed. For the particular study described in this report, the silane film thickness determined by difference between the reacted and bare oxide films was 10 $\pm$ 0.8 nm, indicating binding of the reagent. While the thickness is somewhat greater than expected, the functionality of the reagent assures that

the coverage would not exceed a monolayer; furthermore, the uncertainty reported above does not account for the effects of surface roughness.[14]

RESULTS AND DISCUSSION

ATR Surface Selectivity

The rapid decay of the evanescent wave in attenuated total reflectance is a valuable attribute for its application in measuring interfacial reactions. Confining the intensity of radiation to the interface greatly reduces interferences from solution phase species. The depth of penetration of the radiation beyond an interface, d_p (the distance where intensity drops by a factor of e^{-2} or 14% of its value at the interface) depends on the angle of incidence, θ, the refractive indices of the substrate, n_1, and the overlayer, n_2, and the vacuum wavelength of the radiation, λ, and is given by:[17]

$$d_p = \frac{\lambda}{2\pi n_1 \left[\sin^2\theta - (n_2/n_1)^2\right]^{1/2}} \qquad (1)$$

To evaluate this equation for the conditions of these experiments, the infrared wavelength dependence of the indices of refraction for silicon, fused silica, and the solvent were obtained from the literature.[18-20] A three-layer reflection problem can be solved, by evaluation of the double boundary problem.[21] Fortunately, for amorphous silica, carbon tetrachloride, and cyclohexane, the refractive indexes of these materials are the same within $\pm$ 3% over the wavelength range of interest except where the C-H absorbance bands are found in the hydrocarbon where the deviation is about 10%. As a result, these layers are indistinguishable, and the total internal reflection, therefore, can be analyzed using Equation 1, where the exponential decay of the evanescent wave begins at the silicon/silica interface. Using Equation 1, the literature values for refractive indices, and the angle of incidence, $\theta = 46.29^\circ$, the depth of penetration beyond the silicon-silica interface as a function of wavelength was calculated . Since the wavelength variation of the refractive indeces of the silicon substrate, oxide, and solvent are weak, the penetration depth of the radiation beyond the interface is linear with wavelength except for small deviations in the C-H stretching region. The values of d_p into carbon tetrachloride and cyclohexane are nearly the same, and range

from around 2000 A at 2.6 μm to 4500 A at 5.8 μm.

A larger background from solution-phase absorbance with increasing penetration depth is a consideration in this work, but there is a counter-running, sensitivity trade-off to be considered. When examining absorbers at the silica-solution interface, background radiation reflected from the low-index, silica layer does not sample the silica solution interface and reduces sensitivity. This problem was tested[15] by comparing ATR-FTIR absorption spectra of 1-hexene in carbon tetrachloride using the silicon ATR plate with and without an oxide layer. The loss of absorbance sensitivity can be modeled by accounting for the radiation reflected from the silicon-silica interface and the correspondingly lower intensity which samples the solution absorbance. This model accurately predicts the transmittance measured in the presence of oxide.[15] From the loss of sensitivity, an estimate can be made of the oxide thickness, which is only 18% larger than the value determined by ellipsometry.

ATR Measurement of Surface Reaction Kinetics

Confinement of the evanescent field intensity by total internal reflectance to the interfacial region not only reduces the sensitivity to solution phase species, but also allows one to quantitatively measure changes in concentration at the interface of a molecule which adsorbs or covalently binds to the surface. To test this measurement concept, consecutive infrared spectra were collected with the ATR-FTIR flow cell over the course of a surface derivatization reaction. The silicon substrate had a 94 nm surface oxide film as determined by ellipsometry, and the cell was filled with a solution of 0.043 M solution of diphenylchlorosilane in CCl_4. Using the first spectrum after filling the cell as a reference, difference spectra were gathered over a period of 140 minutes and are plotted from top to bottom in Figure 1.[15] The region of the infrared spectrum shown in the figure contains aromatic C-H stretching peaks above 3000 cm^{-1} as well as Si-H stretching at ~2175 cm^{-1}. Inspection of the Si-H peak shows that it shifts with time, likely due the change in electron density on silicon upon exchange of chlorine with oxygen when the reagent binds. The time scale of the shifting correlates with the covalent binding of a monolayer of silane which cannot be rinsed from the surface by the solvent.

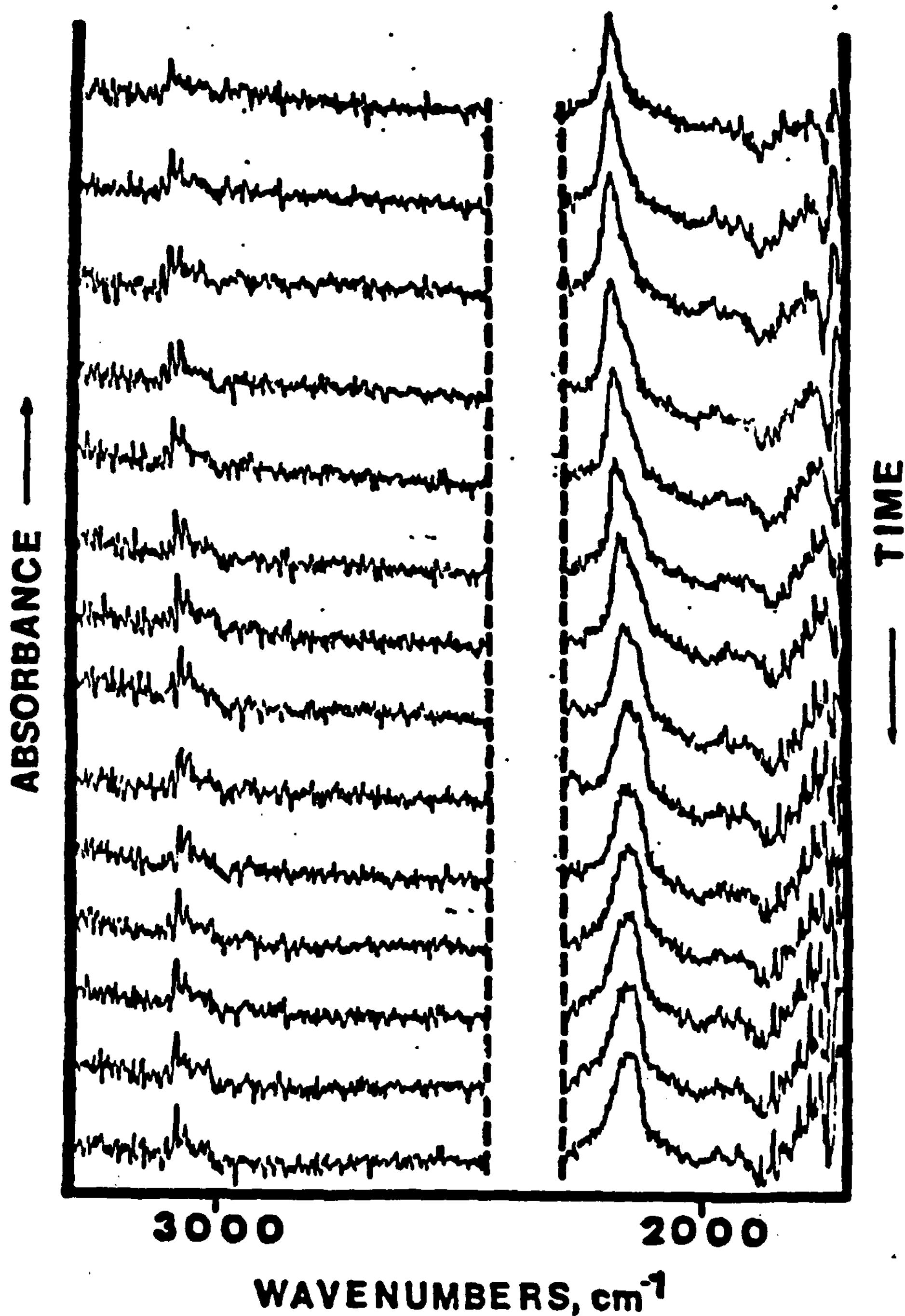

FIGURE 1 ATR difference spectra of the binding of diphenylchlorosilane to silica from CCl_4 solution. Reagent concentration is 0.043 M. The earliest spectrum is at the top; interval between spectra is approximately 5 minutes.

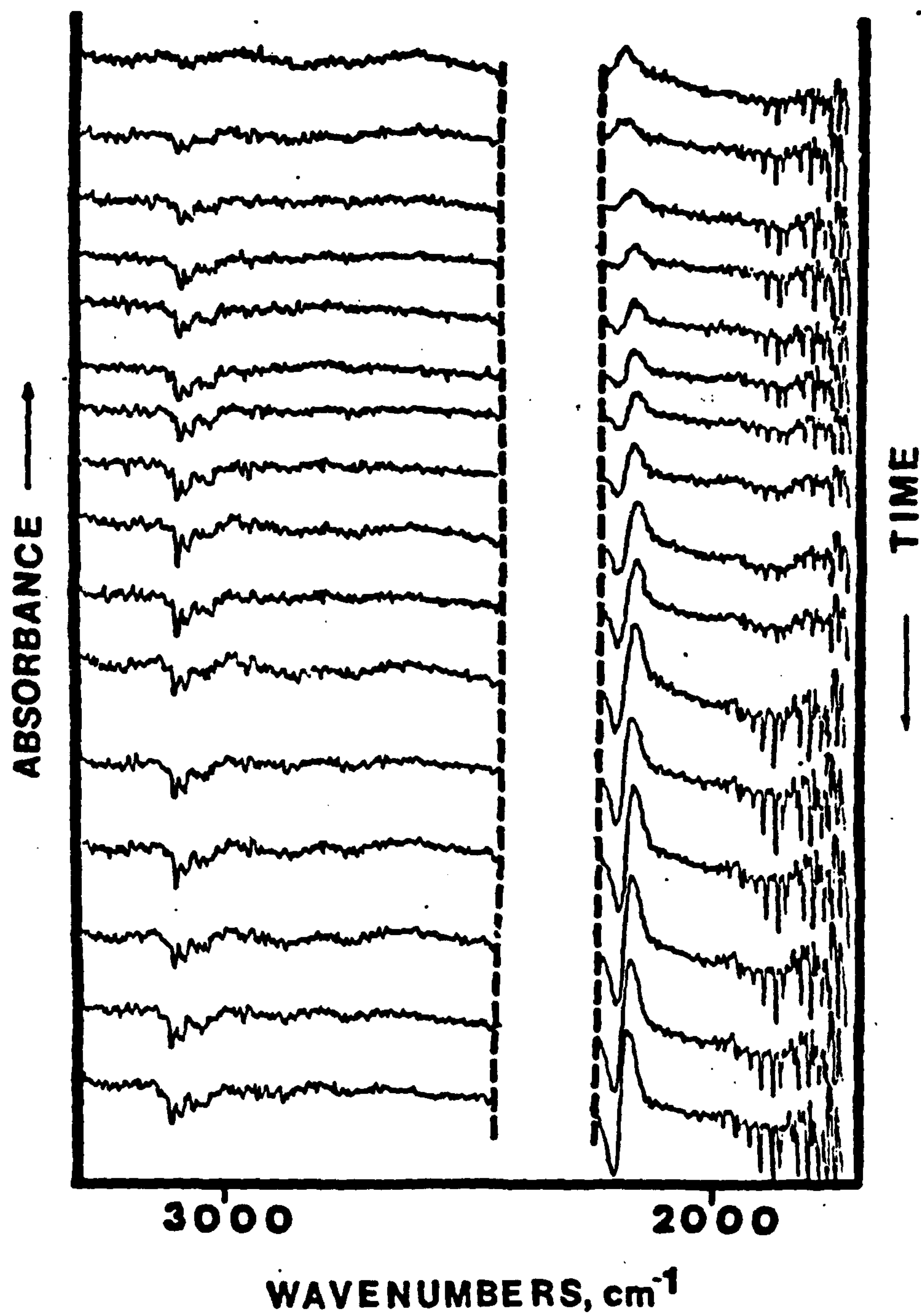

FIGURE 2 ATR difference spectra of silane binding to silica. Reagent concentration is 0.21 M in CCl_4 solution.

The narrower, higher energy Si-H peak shown in the first difference spectrum has a peak frequency which is indistinguishable from the bulk silane spectrum. The fact that a positive absorbance peak is present indicates that the silane concentration at the interface is higher than when the initial background spectrum was collected. This silane is not covalently bound to the surface since it can be removed by rinsing with solvent. The layer of adsorbed silane apparently organizes at the surface over a period of about 10 minutes, analogous to the behavior of other strongly adsorbed monomolecular layers at solid surfaces.[22] The concentration of this adsorbed silane layer decreases with time as surface concentration of the covalently bound silane nears saturation. This effect is particularly noticeable when the same reaction is run at a higher solution concentration of silane reagent, as shown in Figure 2. Here, the adsorbed reagent layer is completely formed within the time between filling the cell and generation of the first spectrum. The conversion and loss of this layer to the bound form shows up as a dip in the difference spectrum which disappears at a rate equivalent to the formation of the bound layer.

A picture of the surface reaction kinetics begins to emerge from these observations. Following exposure to the reagent, a physisorbed layer of silane forms at the silica interface at rate which is faster at higher concentrations. The structure of this layer results in minimal change of the Si-H vibrational frequency compared with the solution phase, indicating little interaction of this functional group with the surface. On the other hand, associative interactions between aromatic compounds and porous silica have been observed,[6a] which affect the intensities of aromatic C=C vibrational modes. If the phenyl groups on the silane interact strongly with surface silanols, the configuration of adsorbed species on the surface could interfere with the reaction chemistry.[16] Chemical bonding of the silane reagent with the surface is much slower, forming a complete monolayer after about 90 minutes at a rate which independent of solution concentration of reagent. As the bound surface coverage increases, the concentration of the physisorbed monolayer decreases, the accessibility of surface silanols is reduced by the density of bound silane molecules.

Discussion

The ATR-FTIR method presented here, can readily be applied to determining the kinetics rates of a variety of slow silica/silane reactions. Further investigations and comparisions of the effects of surface pretreatment and catalysts[24] can provide insight into mechanistic details of these reactions. The example system described in this work, where competition between adsorption and reaction were observed, illustrates how real-time spectroscopic data could reveal such information. There are two limitations to this technique as it has been described here. The first limitation is that the time required to collect a spectrum with a tolerable signal-to-noise ratio is approximately five minutes, using the present instrument. The observable reaction rates would not be suitable for experiments with extremely reactive silanes,[25] for example. The second limitation is that the silicon substrate is transparent over a limited spectral region and cuts off below 1600 cm^{-1}. While neither of these limitations is serious for following slow reactions in the functional group IR region, both of the shortcomings are being addressed in our present work by the use of kinetic Raman spectroscopy for studying reactions porous silica samples.[24]

In summary, we have presented a new approach to using a reactive substrate compatible with ATR-FTIR methods to allow the study of kinetics of adsorption and reaction of silica surfaces. Common ATR silicon substrates are oxidized under controlled conditions to generate model silica surfaces. By collecting multiple difference spectra of the system at time intervals following the addition of a silane reagent, one can monitor, in situ, the course of a surface reaction.

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REFERENCES

1. E. M. Eyring and M. E. Wadsworth, Trans. Am. Inst. Mining Met. Engrs. 205, Tech. Publication 4329-B, (1956).
2. Y. J. Chabal in The Structure of Surfaces, Volume 2 of the Springer Series in Surface Sciences. Editors: M.A. Van Hove and S.Y. Tong, New York 1987.
3. M. L. Hair, Infrared Spectroscopy in Surface Chemistry, Dekker, New York, 1967.
4. A. V. Kiselev and J. I. Lygin, Infrared Spectra of Surface Compounds, Wiley, New York, 1975.
5. R. P. Sperline, S. Muralidharan, and H. Freiser, Langmuir, 3, 198 (1987).
6. a) M. L. Hunnicutt, J. M. Harris, and C. H. Lochmüller, J. Phys. Chem., 89, 5246, (1985) b) M. W. Urban, J. L. Koenig, Appl. Spec., 40, 513, (1986).
7. R. T. Graf, J. L. Koenig, and H. Ishida, Anal. Chem., 56, 773 (1984).
8. R. Maoz and J. Sagiv, J. Coll. and Interface Sci., 100, 465, (1984); J. Gun and J. Sagiv, J. Coll. and Interface Sci., 112, 457, (1986); W. D. Bascom, Macromolecules, 5, 792 (1972); N. H. Sung and C. S. Paik Sung, SPI 35th Ann. Tech. Conf. Reinf. Plast., 23-B (1980).
9. R. T. Yank, J. D. Low, G. L. Haller, and J. Fenn, J. Colloid Interface Sci., 44, 249 (1973).
10. M. Kawaguchi, S. Hattori, and A. Takahashi, Macromolecules, 20, 178 (1987).
11. D. J. Kuzmenka and S. Granick, Colloids and Surfaces, 31, 105 (1988).
12. A. Revesz, IEEE Transactions on Electron Devices, 97 (1964).
13. a) K. H. Beckman and N. J. Harrick, J. Electrochem. Soc.: Solid State Science, 118, 614, (1971); b) A. G. Revesz, J. Electrochem. Soc.: Solid-State Science and Technology, 126, 122, (1979).
14. A. H. Carim and R. Sinclair, J. Electrochem. Soc.: Solid-State Science and Technology, 134, 741 (1987).
15. D. B. Parry and J. M. Harris, Appl. Spectrosc., 42, 997 (1988).
16. J. K. Yee, D. B. Parry, K. D. Caldwell, and J. M. Harris, Langmuir, accepted for publication.
17. N. J. Harrick, Internal Reflection Spectroscopy, (Harrick Scientific Corporation, Ossining, New York, 1979) 2nd ed.,p. 30.
18. I. H. Malitson, J. Opt. Soc. Amer., 55 (10) (1965).
19. C. D. Salzberg and J. J. Villa, J. Opt. Soc. Amer. 47, 244 (1957).
20. T. G. Goplen, D. G. Cameron, and R. N. Jones, Appl. Spectrosc., 34, 657 (1980).
21. W. N. Hansen, J. Opt. Soc. Amer. 58, 380 (1968).
22. R. G. Nuzzo, F. A. Fusco, and D. L. Allara, J. Amer. Chem. Soc., 109, 2358 (1987).
23. M. L. Hunnicutt and J. M. Harris, Anal. Chem., 58, 748 (1986).
24. E. P. Pleuddemann, Silane Coupling Reagents, Plenum Press: New York (1982).
24. D. B. Parry, K. R. Wallace, and J. M. Harris, manuscript in preparation.
25. D. E. Williams and T. J. Tangney, in Chemically Modified Surfaces, D.E. Leyden, ed. Gordon and Breach: New York (1986).