J. Am. Chem. Soc. 1991, 113, 9112-9119

Surface Reactions in the Aluminum-Catalyzed Direct Synthesis of Alkylsilanes

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Received February 19, 1991

Abstract: The formation of alkylsilanes (SiR_xH_{4-x}, $x \leq 3$) from the reaction of triisobutylaluminum (TIBA) or 1-iodopropane with an aluminum-promoted silicon surface at 450–600 K under ultra-high-vacuum conditions is reported. With both reactants, alkylsilane production is accompanied by alkene evolution, and in the case of TIBA aluminum deposition. Isotope labeling studies show that the hydrogen atoms in the alkylsilane product come from the β-carbon of the alkyl intermediate generated on the surface by the dissociative chemisorption of the adsorbate. The reaction kinetics implicate β-hydride elimination from alkyls bound to aluminum as the rate-determining step. When this rate-determining step is circumvented by adding atomic hydrogen to the system, alkylsilanes form at temperatures as low as 340 K. Our results show that the presence of metallic aluminum on the silicon surface is critical for (1) dissociatively adsorbing the alkyl iodide or aluminum alkyl, (2) inducing β-hydride elimination of the adsorbed alkyls to form surface hydrogen atoms, and (3) enhancing the diffusion of hydrogen, alkyls, and silicon on the surface.

1. Introduction

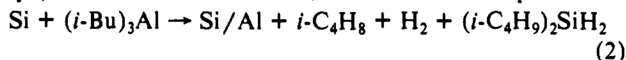
The direct synthesis of organic derivatives of main group metals is an industrially important,[1] historically significant,[2] synthetically useful,[3] and currently relevant[4] class of reactions. Broadly described, direct syntheses of organometallic compounds are those processes which involve the reaction of organic reagents (such as organic halides or hydrocarbons) with a pure element to form organic derivatives of that element.[1,5,6] Frequently, a differing elemental metal is added to the system to reduce the temperature required for reaction and/or modify the product distribution. Since direct syntheses involve heterogeneous reactions between elemental solids and liquid (or vapor phase) organics, the nature of the surface is of central importance.[7] Even so, very little is known about the surface reactions which occur in many of these processes.

This lack of understanding reflects two related factors. Foremost of these is the inherent difficulty in studying surfaces at a molecular level under reaction conditions involving solutions or reactant gases at high pressures. Similarly, the relevant kinetics for many of these systems are such as to make it difficult to induce these reactions under ultra-high-vacuum (UHV) conditions where surfaces are more readily probed. For example, recent studies of the reaction betweem methyl halides (CH_3X) and magnesium[8] or aluminum[9] surfaces under UHV conditions did not produce the Grignard (CH_3MgX) or aluminum sesquihalide (CH_3AlX_2) products that would be expected on the basis of the solution chemistry of these systems.[10,11] It is possible in principle to study certain aspects of the surfaces involved in direct synthesis by transferring the solid between a reactor for catalysis and vacuum for surface analysis (as elegantly demonstrated by Falconer et al. for the copper-catalyzed synthesis of chloroalkylsilanes (eq 1)[12]).

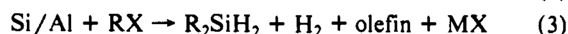
$$Cu_3Si + 2RX \rightarrow R_2SiX_2 + Cu \quad (1)$$

This experimental approach though useful necessarily restricts the development of a complete understanding of the surface reaction mechanism(s) and kinetics involved.

Recently, we have observed that the thermal decomposition of triisobutylaluminum (TIBA) on silicon substrates to deposit aluminum films is accompanied by the evolution of alkylsilanes (SiR_xH_{4-x}, $x \leq 3$) (eq 2).[13] We have since found, as described here, that alkylsilanes can also be formed by reacting suitable alkyl iodides with silicon at 500–600 K in the presence of aluminum (eq 3). As we will demonstrate, the aluminum is important for dissociatively adsorbing the aluminum alkyl or alkyl iodide and for further providing a substrate on which surface alkyls and hydrogen atoms can diffuse via weakly activated processes to silicon atoms which diffuse to the surface of the aluminum overlayer. These heterogeneous reactions are apparently similar to those occurring in patented processes for the bulk synthesis of alkyl- and chloroalkylsilanes from alkylaluminum chlorides (or alkyl chlorides) and silaceous materials.[14] The present finding that alkylsilanes can be obtained at low pressures suggests this system as being an intriguing candidate for mechanistic studies of the surface reactions involved in direct organometallic synthesis. Such studies are the subject of this paper.



$$Si + (i\text{-Bu})_3Al \rightarrow Si/Al + i\text{-}C_4H_8 + H_2 + (i\text{-}C_4H_9)_2SiH_2 \quad (2)$$



$$Si/Al + RX \rightarrow R_2SiH_2 + H_2 + \text{olefin} + MX \quad (3)$$

2. Experimental Section

One Si(100) and four Si(111) single-crystal samples (B-doped, p-type 8–20 Ω·cm) were used in these experiments. The methods of sample preparation and cleaning, as well as the experimental procedures, are discussed in detail in refs 13 and 15. Thin aluminum films (0–10 monolayers (ML)) were evaporated onto the silicon substrates in situ by heating a tungsten filament wrapped around an aluminum pellet (Alpha, 99.999%). The deposition rate used was ~0.01 ML/s, and the aluminum coverage was monitored by Auger electron spectroscopy (AES) and

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(1) For example, the copper-catalyzed synthesis of chloroalkylsilanes (Rochow process): Rochow, E. G. *J. Chem. Educ.* **1966**, *43*, 58.
(2) Victor Grignard won the Nobel Prize in chemistry in 1912 for his RMgX reagent formed by reacting an alkyl halide with magnesium.
(3) For example, the Simmons-Smith reaction: Simmons, H. E.; Smith, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 4256. LeGoff, E. *J. Org. Chem.* **1964**, *29*, 2048.
(4) The direct synthesis of alkylsilanes during aluminum deposition from aluminum alkyls is a potentially detrimental silicon etching reaction in microelectronics manufacturing: Sze, S. M. *Semiconductor Devices: Physics & Technology*; John Wiley: New York, 1985.
(5) Massey, A. G.; Hamphries, R. E. *Aldrichim. Acta* **1989**, *22*, 31.
(6) Rieke, R. D. *Science* **1989**, *246*, 1260.
(7) See for example: Rieke, R. D.; Rhyne, L. D. *J. Org. Chem.* **1979**, *44*, 3445. Burns, T. P.; Rieke, R. D. *J. Org. Chem.* **1987**, *52*, 3674.
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(10) See for example: Hill, C. L.; Vander Sande, J. B.; Whitesides, G. M. *J. Org. Chem.* **1980**, *45*, 1020. Rogers, H. R.; Hill, C. L.; Fujiwara, Y.; Rogers, R. J.; Mikkell, H. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 217.
(11) Grosse, A. V.; Mavity, J. M. *J. Org. Chem.* **1940**, *5*, 10–6. Adkins, H.; Scanley, C. *J. Am. Chem. Soc.* **1951**, *73*, 2854.
(12) Frank, T. C.; Falconer, J. L. *Langmuir* **1985**, *1*, 104. Agarwala, J. P.; Falconer, J. L. *Int. J. Chem. Kinet.* **1987**, *19*, 519. Margrini, K. A.; Gebhard, S. C.; Koel, B. E.; Falconer, J. L. *Surf. Sci.*, in press.
(13) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *Mater. Res. Soc. Symp. Proc.* **1988**, *101*, 177.
(14) Anderson, R. C. U.S. Patent 2,914,549, Nov. 24, 1959. Shlihara, I.; Iyoda, J.; Takahashi, H. U.S. Patent 3,004,053, Oct. 10, 1961.
(15) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Am. Chem. Soc.* **1989**, *111*, 1634.

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low-energy electron diffraction (LEED). We find that growth is layer-by-layer and epitaxial up to ~3 ML, in agreement with published results.[16] The Auger data also reveal that the Al–Si interfaces formed are highly reactive. Interdiffusion is found to occur with only moderate annealing (<500 K). Thus, in the experiments reported here where the evaporated films were heated to 800 K, the surface phase present in these materials is an alloy film of Si in aluminum. In the temperature programmed desorption (TPD) studies, the thermal ramps used were identical to the initial sample annealing cycle in order to minimize any changes in the sample surface composition during the experiment. The aluminum coverages represent the number of monolayers of metal deposited *prior* to annealing as calibrated by monitoring the Si $L_{2,3}VV$ AES peak at 92 eV. AES measurements were performed using a single-pass cylindrical mirror analyzer with an incident energy of 3 kV and a modulation voltage of 2 V peak-to-peak.

Thick polycrystalline aluminum films (>1000 Å) were deposited in an external evaporator and exposed to air prior to insertion into the vacuum system. Extensive sputtering was required to remove the resulting native oxide from these surfaces.

Reagents were obtained from the following sources: Ar, Ne, and hydrogen (Matheson, 99.995%), 1-iodopropane (Aldrich, >99%), 1-iodopropane-*2,2*-d_2 (MSD Isotopes, 99 atom % D), triisobutylaluminum (Alpha, 95.7 and 99.99%), and diisobutylsilane (Petrarch). Initial preparation/purification and dosing of the triisobutylaluminum has been described.[15] The alkyl iodides were purified by several freeze/pump/thaw cycles, passed through an in-line alumina plug to remove HI,[17] and dosed by backfilling the chamber. Hydrogen was passed through a liquid nitrogen trap before introduction into the vacuum chamber; hydrogen atoms were created in situ using a hot (~2500 K) tungsten filament. Gas exposures *were not* corrected for varying ionization gauge sensitivities.

3. Results and Interpretation

We present and interpret our results in three parts. In the first we examine the formation of alkylsilanes of the general structure $(i\text{-}C_4H_9)_{4-x}SiH_x$ formed via the aluminum-catalyzed reaction of triisobutylaluminum with a silicon surface. Second, we demonstrate that aluminum overlayers also promote alkylsilane formation when alkyl iodides are employed as a reagent and, using isotopically labeled iodopropane, delineate the nature of the surface reaction mechanism involved. In the final section, we present studies in which co-adsorbed hydrogen atoms are reacted with iodopropane on an aluminum-covered silicon surface. These latter results are used to confirm the nature of the rate-determining step in various limiting kinetic regimes.

1. Catalytic Formation of Alkylsilanes from Triisobutylaluminum and Aluminum-Promoted Silicon. Triisobutylaluminum is unreactive (reactive sticking probability <0.01) on clean silicon surfaces at temperatures below 600 K.[13] When aluminum is present on the surface, reactions ensue at temperatures as low as 450 K.[15,18] The major reaction pathway followed results in the deposition of aluminum with the concomitant evolution of isobutene and hydrogen. As has been noted in an earlier report, we also find that alkylsilanes are produced during this deposition.[13] This phenomenon is illustrated by the data shown in Figure 1. The mass spectrum shown in Figure 1A is one typically obtained for TIBA scattering from an Al/Si surface held at 300 K; it corresponds to unreacted triisobutylaluminum.[15] The low-mass region (below *m/e* 70) is dominated by ions from the isobutyl ligands of the adsorbate[19] and has been omitted for reasons of clarity. The ions for the major aluminum-containing fragments are seen at *m/e* 198, 141, 99, and 85.

When an aluminum-covered Si surface (the aluminum in this case was deposited on Si(100) by dosing 300 L of TIBA at 850 K followed by 1000 L of TIBA at 550 K to produce a surface with an Al_{67ev}:Si_{92ev} AES ratio of 60) is heated to 550 K while TIBA is impinged onto it, several major changes are evident in the mass spectra measured for the scattered/desorbed flux. First,

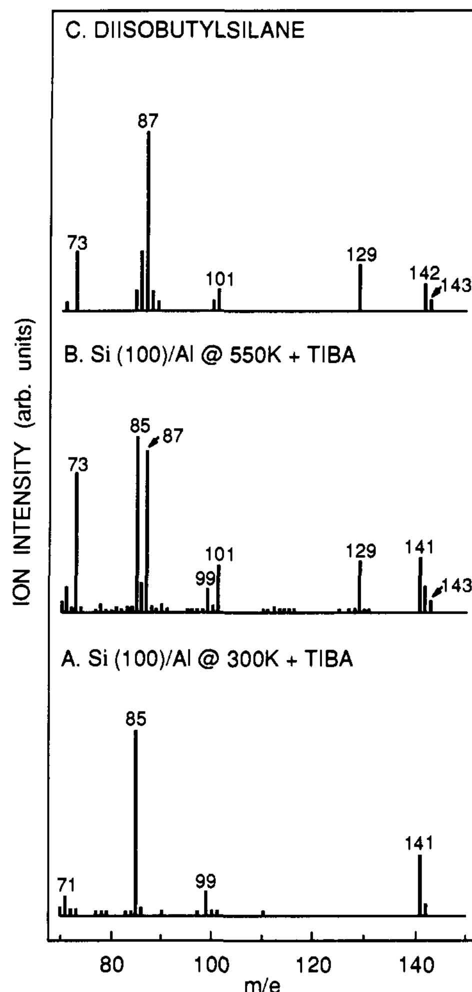

Figure 1. Mass spectra of the species which scatter/desorb when triisobutylaluminum is impinged at an effective pressure of 10^{-6} Torr onto an aluminum-precovered Si(100) surface prepared as described in the text. In A, where the surface is held at room temperature, the mass spectrum corresponds to that of unreacted triisobutylaluminum. In B, the surface has been heated to 550 K, and the data suggest production of predominantly diisobutylsilane whose mass spectrum is shown for comparison in C. Specific assignments are discussed in the text.

the relative size of the peak at *m/e* 56, and similarly for the other cracking fragments of isobutene, increases. Second, the intensities of the aluminum-containing ions decrease significantly (see below). Third, new peaks that are consistently 2 amu heavier than the aluminum-containing ions evident in the data in Figure 1A are observed. A representative example of such a spectrum is shown in Figure 1B. The data shown are uncorrected for the contribution of TIBA present in the background. All of the changes noted above must be due to *surface* reactions, since the TIBA molecules impinge onto the surface under collisionless conditions and the products are detected line-of-sight with a mass spectrometer. The increase in isobutene[20] and the decrease in the aluminum-containing fragments result from the well-documented chemical vapor deposition of aluminum.[15,21] The additional masses detected in Figure 1B and their relative intensities are approximately the same as those measured with the same mass spectrometer and shown in Figure 1C for a background pressure of 5×10^{-7} Torr of diisobutylsilane (MW = 144). This product is indicative of a surface transmetalation reaction in which isobutyl groups are transferred from aluminum to silicon with hydrogen atoms sat-

(16) Lander, J. J.; Morrison, J. *Surf. Sci.* **1964**, *2*, 553.
(17) Bent, B. E.; Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1991**, *113*, 1137, 1143.
(18) Bent, B. E.; Nuzzo, R. G.; Dubois, L. H. *J. Vac. Sci. Technol. A* **1988**, *6*, 1920.
(19) Some of the signal below *m/e* 56 also comes from isobutene which is always present in the incident TIBA flux because of the equilibrium between triisobutylaluminum and diisobutylaluminum hydride.[15]

(20) Butene isomers are difficult to distinguish by mass spectrometry. We presume that the isomer here is isobutene based on the demonstrated β-hydride elimination chemistry for propyl groups adsorbed on aluminum.[15,17]
(21) Cooke, M. J.; Heinecke, R. A.; Stern, R. C.; Maes, J. W. C. *Solid State Technol.* **1982**, *25*, 62; *Solid Films* **1984**, *114*, 367. Levy, R. A.; Green, M. L.; Gallagher, P. K. *J. Electrochem. Soc.* **1984**, *131*, 2175.

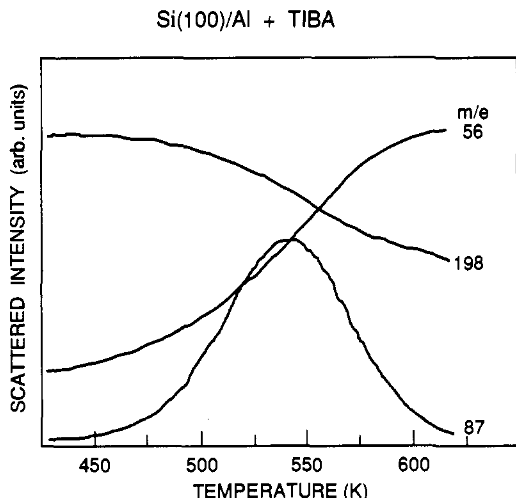

Figure 2. Mass spectrometer ion intensities as a function of surface temperature during the steady-state reaction of triisobutylaluminum with the same aluminum-covered Si(100) surface of Figure 1. *m/e* 56 corresponds to isobutene, a product of the thermal decomposition of TIBA (MW = 198). *m/e* 87 results from the formation of diisobutylsilane. The effective pressure of triisobutylaluminum at the surface in these experiments is about 5×10^{-6} Torr. The source temperature was 323 K.

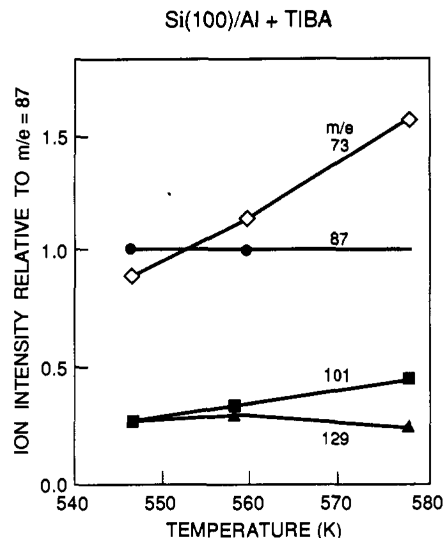

Figure 3. Alkylsilane ion intensities normalized to *m/e* 87 as a function of surface temperature when triisobutylaluminum is scattered from an aluminum-covered silicon surface. The data were obtained by acquiring entire mass spectra (*m/e* 75–145 amu) at each temperature analogous to Figure 1B. We attribute *m/e* 87 (○), 101 (■), and 129 (△) to diisobutylsilane, while *m/e* 73 (▲) probably has contributions from both diisobutylsilane and isobutylsilane.

urating the residual valences (these same ions are not observed when TIBA is reactively scattered from a single-crystal aluminum surface). The close correspondence of the data to this standard suggests that the dominant silicon-containing reaction product is the dialkylsilane $(i\text{-}C_4H_9)_2SiH_2$, although lesser quantities of the monoalkylsilane may be present in the scattered flux as well (see below).

The temperature dependence of the formation of the alkylsilane reaction products is shown in Figure 2. These profiles represent steady-state reaction rates as a function of surface temperature and can be reproduced with little hysteresis either by heating or cooling the surface under a TIBA flux. As shown, triisobutylaluminum (as monitored by *m/e* 198) begins to react at a significant rate on an aluminum-promoted Si surface at ~450 K. Isobutene (*m/e* 56) and alkylsilane (as monitored by *m/e* 129) production also start at ~450 K. The particular data shown in the figure were obtained on the same Si(100)/Al surface which was described above. Note that the yield of isobutene increases and plateaus, while alkylsilane production peaks at ~550 K and then decreases. The behavior of both *m/e* 198 and 56 is characteristic of aluminum chemical vapor deposition, for which similar profiles have been described previously for the reaction of TIBA with single-crystal aluminum surfaces.[15,22] The decrease in alkylsilane production at high temperatures will be addressed in the Discussion section. The general trends seen in the figure are obtained on surfaces varying widely in their initial aluminum coverage, suggesting a facile interdiffusion of Si into the Al overlayer.

All of the alkylsilane masses detected (including *m/e* 143, 129, 101, 87, 73, 59, 45, and 31) show maximum rates of formation in the range of 500–600 K. The peak temperature found in the reactive scattering studies is not the same for all of these ions, however (see Figure 3) In order to avoid effects due to changing surface conditions (which occur gradually during the experiments shown in this figure[23]), complete mass spectra were acquired at each surface temperature. To compensate for small changes in TIBA flux between experiments, intensities at each temperature have been ratioed to that for *m/e* 87. Thus, a constant profile as a function of temperature indicates a profile analogous to that for *m/e* 87. It is evident from Figure 3 that not all ions have the same temperature dependence. While the cracking pattern for a single molecular species could vary as a function of surface temperature due to differing amounts of internal energy,[24] the large percentage change in these signals over a small temperature range (~30 K) argues against this effect and suggests that *at least* two different alkylsilanes, ones whose relative yields vary as a function of surface temperature, are being produced.

While we cannot definitively identify all of the alkylsilanes produced using this data in Figure 3, several products appear likely. On the basis of the observation that the heaviest alkylsilane mass we observe is 143, we presume that the largest alkylsilane of *significant abundance* is diisobutylsilane (MW = 144). This species can account for the similar temperature profiles at *m/e* 129 (△), 101 (■), and 87 (○). The increase in the ratio of *m/e* 73 (▲) to 87 as a function of temperature is believed to reflect an increase in the relative amount of isobutylsilane $(RSiH_3)$ present in the product mixture (*m/e* 87, a major ion in the cracking pattern of diisobutylsilane (Figure 1), does not have significant intensity in the cracking pattern of isobutylsilane[25]). That the monoalkylsilane product should dominate at the higher temperatures seems reasonable, given that the steady-state coverage of isobutyl groups on the surfaces decreases with increasing surface temperature (see the Discussion section). We have previously suggested that the slight increase in *m/e* 101 relative to 87 could be due to the formation of $H_2Si(CH_3)(C_4H_9)$ at higher temperatures as a result of β-methyl elimination by the adsorbed isobutyl groups.[13] This suggestion is supported by the observed ionization cracking pattern of the authentic silane measured in independent control experiments.

Thermal desorption experiments provide further insight into the relevant processes involved in the formation of the various alkylsilanes. Figure 4 shows the product desorption as monitored by the *m/e* 56 (isobutene) and 87 (diisobutylsilane) ions after adsorbing a saturation coverage of TIBA at 350 K onto a Si(111) surface precovered with 0.65 ML of evaporated aluminum.

(22) Bent, B. E.; Dubois, L. H.; Nuzzo, R. G. *Mat. Res. Soc. Symp. Proc.* **1989**, *131*, 327.

(23) Continued aluminum deposition can inhibit silicon diffusion to the surface, while carbon incorporation may occur for depositions at temperatures above ~600 K.

(24) McLafferty, F. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980; Chapter 7.

(25) When isobutylsilane is not commercially available, *n*-hexylsilane (MW = 116) was purchased and studied. Masses 114–116 are all small in the cracking pattern (<2% of the parent peak), and of these ions, M − 2 (114, corresponding to loss of H_2) is the largest. We therefore expect M − 2 (*m/e* 86) rather than M − 1 (*m/e* 87) to predominate for isobutylsilane. Presumably *m/e* 73 has significant contributions from both diisobutyl- and isobutylsilane.

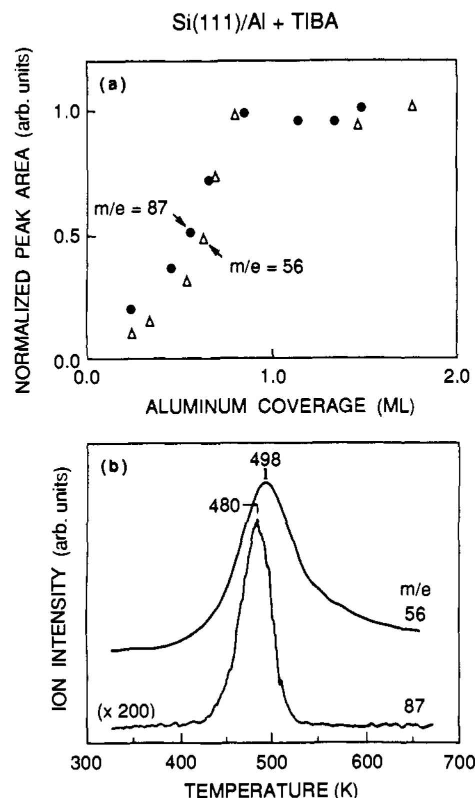

Figure 4. (a) Thermal desorption of isobutene (as monitored by m/e 56) and diisobutylsilane (as monitored by m/e 87) after adsorbing a saturation coverage of triisobutylaluminum at 350 K onto a Si(111) surface precovered with 0.65 ML of evaporated aluminum and flashed to 800 K. The heating rate was 6 deg K/s. (b) The relative amount of both products (determined by integrating the thermal desorption peak area) as a function of aluminum surface coverage.

Spectra similar to that for m/e 87 are obtained for all the alkylsilane masses denoted with arrows in Figure 1B. The comparison in Figure 4 between the rates of formation of isobutene and diisobutylsilane shows that, analogous to the results of experiments conducted under steady-state conditions (Figure 2), both products begin to form at about 400 K. The evolution of diisobutylsilane peaks, however, at a slightly lower temperature. The relative yields of these products appear to be roughly constant as a function of aluminum coverage as indicated by the insert. We also find that neither product forms without aluminum being present on the surface and that the yields of both products saturate at ~1 ML coverage of aluminum.

The dependence of the diisobutylsilane product yield on the TIBA exposure is shown in Figure 5. It is significant to note that the alkylsilane desorption temperature is nearly constant as a function of TIBA dose. This observation strongly suggests that a first-order process, such as the decomposition of surface alkyl groups to produce hydrogen atoms, is the rate-determining step. This assertion is confirmed by the atomic hydrogen coadsorption studies discussed later in subsection 3.

2. Alkylsilane Production from Alkyl Iodides and Aluminum-Promoted Silicon. We have shown in previous studies that many alkyl iodides dissociate below 200 K on aluminum surfaces to form adsorbed alkyl groups and co-adsorbed iodine atoms.[15] In the present study, we have utilized the surface alkyl groups derived from the decomposition of alkyl iodides to study the mechanism of the formation of alkylsilanes. Alkyl iodides are particularly useful in such studies since they can be readily labeled with deuterium. The results discussed here will focus on 1-iodopropane and 1-iodopropane-*2,2-d*$_2$; similar results have also been found for 1-iodo-2-methylpropane.

In the absence of aluminum, no organosilicon products of any sort are formed as a result of the adsorption of alkyl iodides on silicon under ultra-high-vacuum conditions. For example, 1-iodopropane desorbs molecularly from a clean Si(111) surface below 300 K. When aluminum metal is present on the surface, however, several new products, including propylene, hydrogen, and various alkylsilanes, are formed. TPD profiles of propylene and alkylsilane evolution from the decomposition of 1-iodopropane on an aluminum-covered silicon surface are shown in Figures 6 and 7. In these experiments, 1-iodopropane was adsorbed at 320 K onto a Si(111) surface precovered with ~5 ML of Al (the surface was annealed prior to the adsorption by flashing the sample to 800 K). The dose dependence of propylene evolution shown in the inset of Figure 6 has the general shape (although not the explicit functional form) expected for Langmuir adsorption. In Figure 7, the intensity of the ion at m/e 73 [$H_2Si(propyl)^+$] is

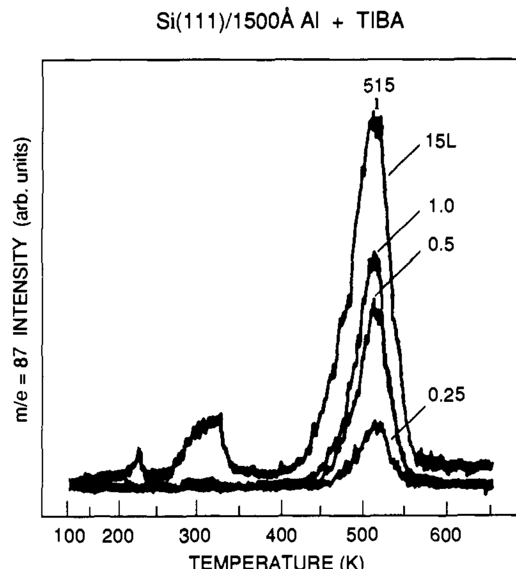

Figure 5. Desorption of diisobutylsilane (as monitored by m/e 87) as a function of triisobutylaluminum dose onto a Si(111) surface pre-covered with ~1500 Å of evaporated aluminum. The lack of shift in the desorption peak temperature as a function of coverage suggests a first-order process. The heating rate was 7.5 deg K/s.

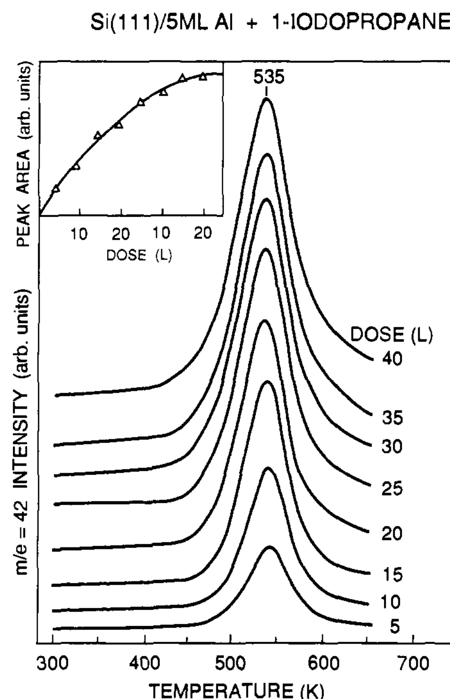

Figure 6. Propylene desorption as a function of 1-iodopropane dose at 320 K onto a Si(111) surface precovered with 5 ML of aluminum evaporated at 300 K and flashed to 800 K. The heating rate was 8 deg K/s. The insert shows the integrated TPD peak area as a function of iodopropane dose.

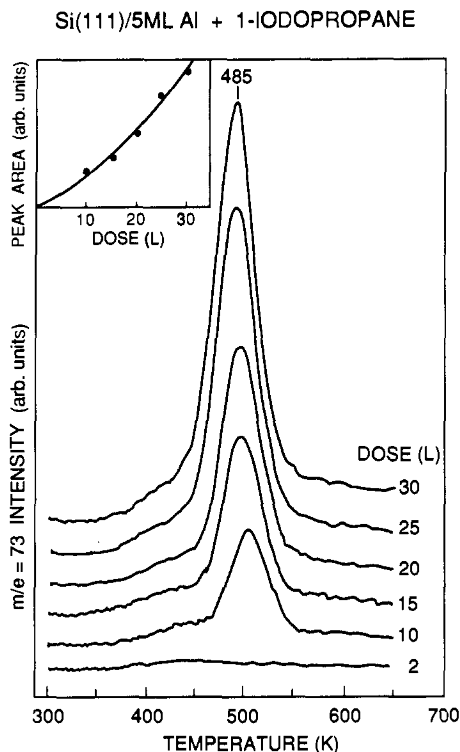

Figure 7. Dipropylsilane desorption (as monitored by m/e 73) as a function of 1-iodopropane dose at 320 K onto a Si(111) surface precovered with 5 ML of aluminum evaporated at 300 K and flashed to 800 K. The heating rate was 8 deg K/s. The insert shows the integrated TPD peak area as a function of iodopropane dose.

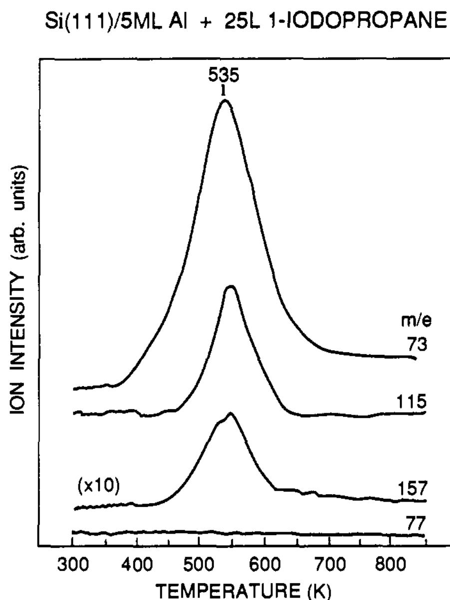

Figure 8. Ions characteristic of propylsilanes monitored during 1-iodopropane thermal decomposition on a Si(111) surface precovered with 5 ML of aluminum evaporated at 300 K and flashed to 800 K. m/e 73 corresponds to $(C_3H_7)SiH_2^+$ while m/e 115 is due to $(C_3H_7)_2SiH^+$. The heaviest ion (m/e 157) is characteristic of either $(C_3H_7)_3Si^+$ or SiH_2^+. The heating rate was 5 deg K/s.

plotted as a function of iodopropane exposure, and the coverage dependence of the yield (which is different from that for propylene) is plotted in the inset. In addition to the monoalkylsilane cracking fragment at m/e 73, we have also monitored the evolution of di- and trialkylsilanes as illustrated by the data plotted in Figure 8. We note, however, that the ion m/e 157 may correspond to either $(propyl)_3Si^+$ or $ISiH_2^+$ (see below). In either case, the relative quantity of trialkylsilanes produced is small and, further, ions corresponding to tetraalkylsilane products are not detected. The

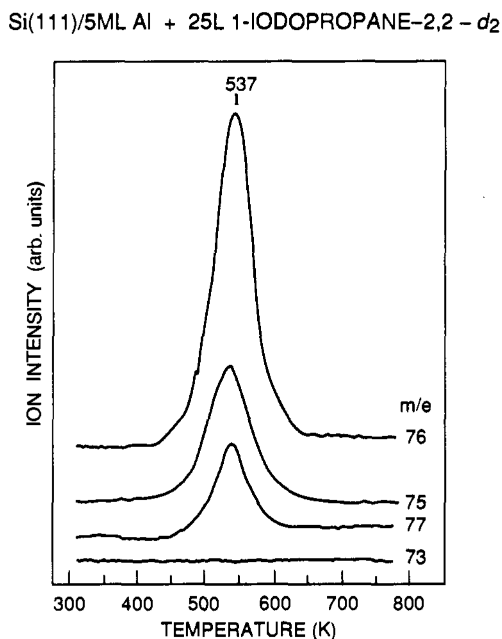

Figure 9. Desorption of partially deuterated alkylsilanes after adsorbing 25 L of 1-iodopropane-$2,2$-d_2 onto a Si(111) surface precovered with 5 ML of aluminum evaporated at 300 K and flashed to 800 K. The heating rate was 5 deg K/s.

major point of note in these experiments is that both the product alkene and alkylsilanes are produced at approximately the same temperature. Further comment on this point is deferred to the Discussion section.

We have failed to find other definitive evidence of the desorption of halogen-containing products. If present, they appear to be a minor species. The thermal ramps shown in the figures are sufficient to deplete the surface of iodine atoms (as determined by AES). We know from other studies that Al–I fragments will desorb at temperatures above 600 K.[17] We suspect that similar reactions may also occur for the aluminum-covered silicon surfaces as well (bond energy arguments suggest that the retention of the halogen atom by aluminum is thermodynamically favored). Further refinement (in particular a significant increase in sensitivity at high values of m/e) of the mass spectral methods used will be necessary to clarify this point. This ambiguity notwithstanding, the data strongly support the mechanistic notions developed from the non-halogen-containing TIBA reagent.

To confirm that the hydrogen atoms required to form alkylsilanes come from β-hydride elimination reactions of surface alkyl groups, the decomposition of 1-iodopropane-$2,2$-d_2 was studied. Previous experiments with this adsorbate have shown that propyl groups produced by low-temperature carbon–iodine bond dissociation on aluminum surfaces decompose at 500 K by β-deuterium elimination to produce propylene-d_1.[15,17] When silicon is present, these surface D atoms might also combine with Si and unreacted propyl groups to form partially deuterated propylsilanes. To obtain the data presented in Figure 9, we monitored the production of partially deuterated silanes when 1-iodopropane-$2,2$-d_2 was decomposed on an aluminum-covered silicon surface. While it is not possible to assign all of these cracking fragments to a single molecular species, it is clear that all ions above m/e 74 are due to deuterium incorporation in the product alkylsilane (none of these masses is observed with non-detuerated 1-iodopropane). Particularly significant is the presence of m/e 77, an ion which corresponds to $(C_3H_5D_2)SiD_2^+$. This ion is a likely cracking fragment of $(C_3H_5D_2)_2SiD_2$, indicating that both the alkyl and the deuterium atoms in the alkylsilane come from the iodopropane.[26]

3. Effect of Surface Hydrogen Atoms on Alkylsilane Production. To test the hypothesis that the formation of alkylsilanes from either

(26) The presence of m/e 76 is puzzling and may indicate impurity hydrogen atoms on the surface or in 1-iodopropane-$2,2$-d_2.

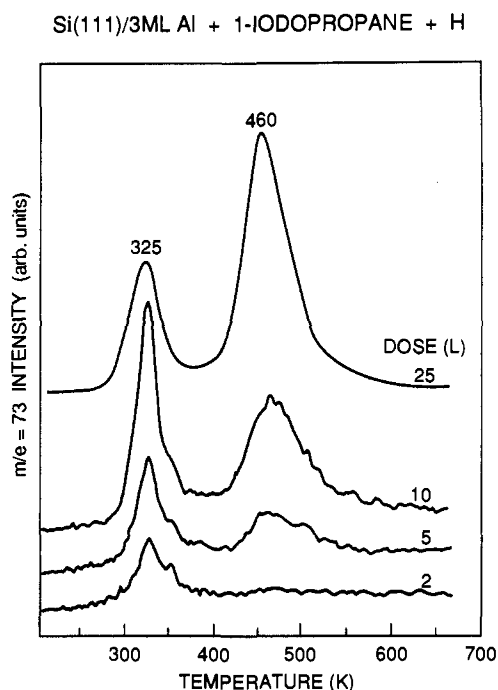

Figure 10. Alkylsilane desorption (as monitored by *m/e* 73) from a Si(111) surface covered by ~3 ML of aluminum (after adsorbing the indicated amounts of 1-iodopropane the surface was saturated with atomic hydrogen).

TIBA or alkyl iodides is limited by the availability of surface hydrogen atoms, we generated hydrogen atoms on aluminum-covered silicon at low temperature by evaporating them from a hot tungsten filament. Previous studies have shown that hydrogen atoms undergo two reactions on aluminum-covered silicon: recommendation to give H_2, and reaction with surface silicon atoms to evolve silane (SiH_4).[27] Both processes occur at about 340 K.

When 1-iodopropane is co-adsorbed with hydrogen atoms on aluminum-covered silicon (θ_{Al} = 3 ML, annealed at 800 K), alkylsilanes are also produced. The results of such studies are shown in Figure 10. Two alkylsilane (*m/e* 73) desorption peaks are evident at 325 and 460 K. The 460 K peak corresponds to that found in the absence of co-adsorbed hydrogen atoms, while the 325 K peak results from the influences of the co-adsorbed hydrogen. As expected, the relative area of the 325 K peak is largest for low 1-iodopropane exposures where the H:alkyl ratio is largest. The presence of this lower temperature peak strongly suggests that the rate-determining step in producing alkylsilanes from aluminum alkyls or alkyl iodides on aluminum-promoted silicon is the formation of surface hydrogen atoms.

4. Discussion

We discuss our results in three parts. First we discuss the nature of the surface reaction mechanism. Next we define the role of aluminum in promoting the reaction, and finally we examine the nature of the surface reaction kinetics.

1. Surface Reaction Mechanism. The present study shows that alkylsilanes (SiR_xH_{4-x}, $x \leq 3$) can be formed at 450–600 K by the reaction of either triisobutylaluminum or an alkyl iodide containing β-hydrogens with aluminum-covered silicon surfaces. The most significant experimental observation is that the reaction is *not* detected in the absence of this metal.[28] It is significant that the organosilane production is accompanied by alkene evolution and that the temperature at which both processes "turn-on" is the same as that at which alkyl groups bound to aluminum surfaces begin to undergo β-hydride elimination at a measurable rate (~450 K). We infer from these facts that the hydrogen atoms in the product alkylsilanes come from the β-elimination of a hydrogen in a surface alkyl intermediate. When hydrogen atoms are made available on the surface at low temperature, alkylsilanes form much more readily (as low as 340 K). These observations along with our previous findings that both alkyl iodides and aluminum alkyls adsorb on aluminum surfaces to produce alkyl groups which are thermally stable up to 400 K[15,17] led us to propose the reaction scheme shown in Figure 11 for the formation of alkylsilanes.

In the upper mechanism of this figure, the rate-determining step we propose is the formation of surface hydrogen atoms by β-hydride elimination reactions of the surface alkyl groups. The energetics of this reaction limit alkylsilane production to temperatures above ~450 K and explain why silane and alkene production occur at the same temperature. When hydrogen atoms are added as shown in the lower mechanism, alkylsilanes will form as low as 340 K. The threshold reaction temperature observed for alkylsilane formation in this case (~300 K) is the same as that for the recombinative desorption of hydrogen from aluminum surfaces.[29] Since it is unlikely that the H + H and Si + H reactions will have identical surface reaction velocities, this result suggests that hydrogen atom diffusion on the surface may in fact be the rate-determining step in these latter processes. Indeed, H atom diffusion has been proposed as the rate-determining step in hydrogen recombination on an Al(100) surface.[29]

The nature of the aluminum/silicon interface shown schematically in Figure 11 is not well-understood. Since alkylsilane production reaches a maximum at ~1 ML of evaporated aluminum (Figure 4) and the activity of the surface does not diminish significantly for thicker films, we show a silicon surface completely covered with aluminum. The positive curvature in Figure 7 for alkylsilane production as a function of aluminum coverage suggests that more than one aluminum atom is required at the active site. A similar inference has been made with regard to the copper-catalyzed formation of chloroalkylsilanes where it is suggested that "metal-rich" sites are needed for catalytic activity.[12] The facile diffusion we observe for silicon to the surfaces of thicker aluminum films to form these "metal-rich" sites is somewhat surprising, given the low solubility (0.8 wt %) and diffusivity ($D = 2 \times 10^{-8}$ cm^2/s) of silicon in aluminum. We suspect that diffusion through these films occurs mainly along grain boundaries. In support of this hypothesis, we have found that silicon diffusion can be slowed by heating thick aluminum films to 800 K, a process which is known to decrease the number of grain boundaries.

2. Role of Aluminum. Aluminum plays a key role in most of the steps discussed above, including the following: (1) dissociation of the alkyl precursor, (2) promoting β-hydride elimination reactions of surface alkyl groups to generate chemisorbed hydrogen atoms, and (3) allowing facile diffusion of alkyl intermediates and hydrogen atoms across the surface. It is also likely that strong kinetic synergisms exist as a result of the placement of silicon atoms in an intermetallic phase rather than in the bulk lattice. These conclusions are based on the following experimental observations. First, neither aluminum alkyls[13] nor alkyl iodides [this work] dissociatively adsorb with significant probability on silicon surfaces, while both dissociate below room temperature on aluminum.[15,17] Second, the fact that the β-hydride elimination rate is virtually the same on aluminum and aluminum-promoted silicon suggests that silicon plays little role in this step of the reaction. Finally, the diffusion of hydrogen atoms and formation of silane, which appears to be extremely slow on silicon surfaces at 500 K,[30]

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(28) In the case of the reaction of triisobutylaluminum with silicon, aluminum will eventually deposit onto the silicon by chemical vapor deposition, although the temperature needed to effect the initial deposition is higher than that necessary for steady-state growth. Upon the nucleation of the metal overlayer, alkylsilanes can be formed.

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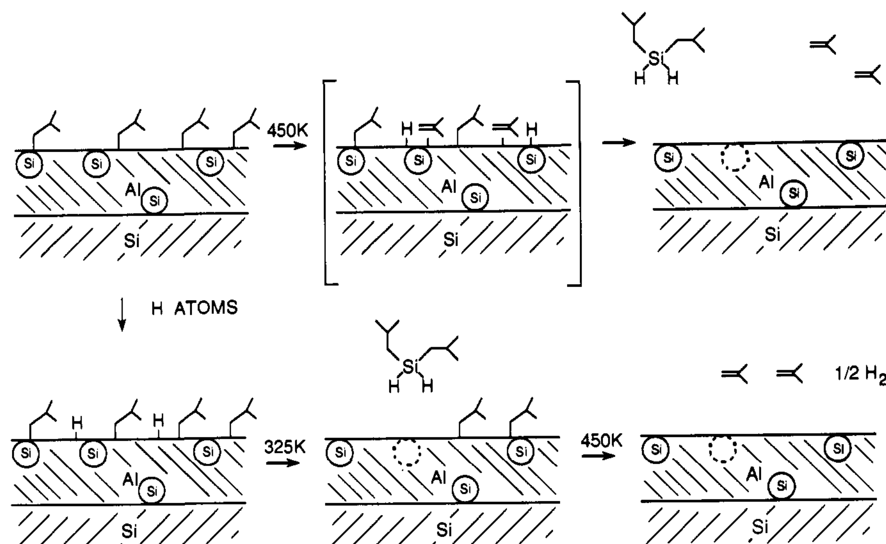

Figure 11. Proposed surface reactions in the aluminum-promoted synthesis of alkylsilanes (SiR_xH_{4-x}) from aluminum alkyls (or alkyl iodides) and silicon. The reactions are illustrated here for isobutyl groups which can be produced by dissociative adsorption of either triisobutylaluminum or 1-iodo-2-methylpropane.

is relatively facile on aluminum (a surface on which hydrogen recombines and desorbs at ~340 K).

3. Surface Reaction Kinetics. We now consider why catalytic alkylsilane production from triisobutylaluminum and aluminum-promoted silicon attains a maximum rate at ~550 K and then decreases at higher temperatures (see Figure 2). In the following discussion, we restrict our analysis to the case of thick aluminum films, a limit in which the surface coverage of metal can be considered to remain approximately constant during the scattering experiment. Under these conditions, the surface coverages of Si, H, and alkyl determine the relative amounts of alkene, hydrogen, and alkylsilane which form. For silicon, both thermodynamic and kinetic considerations[31] suggest that the surface coverage will increase with temperature and therefore favor alkylsilane formation. Conversely, for a constant incident flux of triisobutylaluminum, the surface coverages of both hydrogen and alkyl groups will decrease at high temperature where the flux of TIBA to the surface becomes rate-determining. In Figure 12 we calculate the surface coverage of hydrogen (solid line) and isobutyl groups (dashed line) in the presence of ~10^{-6} Torr of TIBA (approximate pressure of TIBA used in Figures 1 and 2). The calculations are based on a model discussed previously.[15,22] It is noteworthy that the maximum steady-state coverage of hydrogen occurs at ~550 K, which coincides with the maximum alkylsilane formation rate (see Figure 2). This similarly suggests that the surface hydrogen coverage plays a dominant role in determining the rate of alkylsilane formation, an intuitively attractive result. This also provides a simple rationalization of the kinetic profiles inferred for the monoalkylsilanes, the formation of which requiries three consecutive bimolecular surface reactions with adsorbed hydrogen atoms.

The data above also implicitly establish a feature of the kinetics which distinguishes the processes which occur in UHV from those conducted under higher pressure ambients. The silane-yielding reaction channels are found, in the particular case where alkyl halides are employed as adsorbates, to require concomitant β-hydride elimination reactions. Our inability to detect halogen-containing silicon products in the gas phase and the efficient access of reaction channels kinetically coupled to the β-elimination pathway strongly suggest that the barrier for the formation of products of the general structure $R_{4-x}SiI_x$ must be greater for the ~25 kcal/mol barrier to β-hydride elimination on Al.[15,17] It is also clear that features of such reactions, when conducted in non-UHV environments, must be sensitive to surface chemistries

(31) Both the rate of solid–solid interdiffusion and the entropic contribution favoring dissolution will increase at higher temperatures.

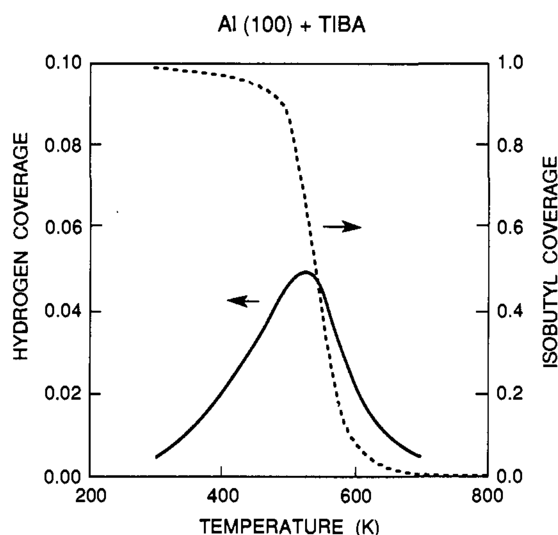

Figure 12. Fractional surface coverages of isobutyl groups (dashed line) and hydrogen atoms (solid lines) during the reaction of triisobutylaluminum with an Al(100) surface. The values plotted were obtained by incorporating the rate of hydrogen desorption into a model developed for aluminum chemical vapor deposition from triisobutylaluminum.[15,22] The key feature is the fact that the coverages of both adsorbates decrease to zero at higher temperatures where the surface reaction rate greatly exceeds the incident flux of triisobutylaluminum.

which are at present still poorly understood. Further experiments will be needed to define the nature of those processes which contribute to these more complicated etching reactions.

5. Conclusions

Our results show that alkylsilanes (SiR_xH_{4-x}, $x \leq 3$) can form in the temperature range of 450–600 K by reacting triisobutylaluminum or alkyl iodides with silicon surfaces precovered with aluminum. Alkenes are evolved in both processes, and the triisobutylaluminum reaction is accompanied by aluminum deposition on the surface. The growing aluminum film does not significantly inhibit alkylsilane production (at least for Al films several hundred angstroms thick) since silicon continues to diffuse through the metal overlayer (presumably along grain boundaries). The rate-determining step in both processes is β-hydride elimination by the alkyl groups bound to the aluminum surface, a reaction yielding the corresponding alkene and surface hydrogen atoms.

Isotope labeling experiments conducted with several *n*-propyl iodides confirm that it is the β-hydrogen atoms of the alkyl group which combine with silicon and other alkyls to form the silane products. When hydrogen atoms are added to the system, alkylsilanes form at temperatures <340 K. It appears that the rate-determining process under these conditions is surface diffusion of hydrogen adatoms.

Registry No. Si, 7440-21-3; Al, 7429-90-5; 1-iodopropane, 107-08-4; triisobutylaluminum, 100-99-2; diisobutylsilane, 136425-30-4; isobutene, 115-11-7; isobutylsilane, 18165-87-2; propylene, 115-07-1; dipropylsilane, 871-77-2.

Gas-Phase Ambident Reactivity of Acyclic Enolate Anions

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Abstract: The gas-phase reactions between acyclic enolate anions and unsaturated perfluorocarbon compounds have been studied with use of the method of Fourier transform ion cyclotron resonance. Unsaturated perfluorocarbon compounds react in a characteristic way with either the oxygen or carbon end of an enolate anion to produce distinctive ionic products. The relative yields of ionic products formed in the reactions of a series of ambident acyclic enolate anions of the type $R_1HC{=}CR_2O^-$, reveal the whole spectrum of ambident reactivity from 100% addition via the carbon nucleophilic center up to 99% addition via the oxygen nucleophilic center. There appears to be a correlation between the reaction selectivity and the experimental electron detachment threshold energies, and thus the energy of the HOMO, of the enolate anions. The nature of this correlation suggests that the competition between the reaction channels is controlled by specific frontier orbital interactions of the reactants rather than by the charge distribution in the enolate anions alone.

Ambident ions can be characterized as ions in which reactive sites are connected through mesomerism.[1] The competition between the reactive sites is generally rationalized in terms of orbital versus charge control[2-4] or by making use of the hard and soft concept, which deals with the specific affinities of the atoms which are involved in bond formation.[3,5-7]

Among the ambident ions enolate anions occupy a special position since they play a very important role in synthetic organic chemistry. For this reason considerable effort has been devoted to the controlling factors in the reactions with alkylating agents[1,2,5] such as the influence of the solvent, the temperature, the electrophile, and the counterion.

Most of the charge is thought to be localized on the oxygen atom[4-6,8-10] by which both the solvent and the counterion are favored to associate with this atom[1] thereby shielding it for electrophilic attack. Nonetheless, oxygen alkylation and acylation have been demonstrated to occur in aprotic solvents under conditions where hydrogen bridging and specific solvation of the oxygen were minimized.[1,6]

In order to obtain a better understanding of the intrinsic chemical properties of enolate anions, some research groups have studied enolate anion reactions in the gas phase, where solvent and counterion association is fully eliminated. Under these conditions kinetically favored oxygen alkylation has been found to occur exclusively in the reaction between the enolate anion from cyclohexanone and bromomethane.[11] Yet, it appears from most studies that the gas phase allows a fair competition between the two nucleophilic centers in the enolate anions, in which the properties of both the enolate anion and the substrate seem to play an important role.[12-16]

Gas-phase ion/molecule reactions are typically studied making use of mass spectrometric techniques which in general only allow detection and analysis of the ionic products. Unfortunately, this limitation implies that reaction pathways leading to these product ions cannot be established unambiguously for all reaction systems. Therefore, the reaction between enolate anions and unsaturated polyfluorocarbon compounds is of special interest since it has been demonstrated that addition of oxyanions and carbanions, proceeding via an oxygen[13,15,17-20] and carbon[13,15,21-23] nucleophilic center, respectively, yields distinctive ionic products. On the basis of these probe reactions it has been concluded that in the gas-phase reaction between the acetaldehyde-enolate anion and pentafluoroanisole aromatic substitution proceeds preferentially via oxygen in contrast with the enolate anion of acetone which favors initial addition via carbon.[13] Similarly, the enolate anion of acetic acid is considered to react exclusively via its carbon nucleophilic center with hexafluorobenzene.[24]

Recently, a systematic study has been reported concerning the ambident reactivity of enolate anions in the tube of a flowing afterglow apparatus toward hexafluoropropene.[15] For a series of

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