Reactions of Silicon Clusters with SiD_4: Formation of Structural Isomers

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Bare and partially hydrogenated silicon clusters, $Si_mD_n^+$, react with SiD_4 to produce structural isomers of $Si_2D_2^+$, $Si_3D_4^+$, and $Si_4D_2^+$. These structural isomers are distinguished by their different reaction rates with SiD_4 and by their formation of unique products in these reactions. In addition, other $Si_mD_n^+$ ions are observed to undergo reactions which are endothermic for the ground state. These ions contain excess energy which may be vibrational or, for Si^+ and SiD^+, electronic energy. The relevance of these findings to silane plasma reactors is presented.

Introduction

Silane plasmas are industrially important for the deposition of silicon films. At present the chemical events occurring within the plasma are not totally understood. Efforts are under way to detail the important reactions and correlate the gas-phase processes with improvement in film quality. Several models of the gas-phase and surface reactions in silane deposition have been developed to assess the importance of various parameters.[1-4] An integral part of these models is the involvement of ion/molecule reactions. However, the necessary reaction rates and product distributions with silane are available only for the monosilicon-containing ions, SiH_n^+;[5-8] data for the higher order reactions have been approximated. We have examined in detail numerous higher order ion/molecule reactions.[9,10] In this work we have uncovered evidence for the presence of structural isomers in some of these higher order reactants and products. These isomers are readily differentiated by both reaction rates and products. In addition, reactions of some ions due to the presence of excess internal energy have been identified. Ions with excess energy have a different reaction rate and product distribution. The importance of these findings to silane plasma chemistry and cluster chemistry will be presented.

Experimental Section

A pulsed Nd:YAG laser (typical energies of 5–20 mJ/pulse, 10 ns fwhm, operating at either 1064 or 532 nm) was used to ablate polycrystalline silicon (99.999%; Metron Inc., Allemuchy, NJ) just outside of the trapping cell of a modified Nicolet FT/MS-1000 Fourier transform mass spectrometer (FTMS).[11] The instrument has a differentially pumped dual cell configuration similar to the Nicolet FT/MS-2000. Typical conditions were magnetic field strength, 2.96 T; cell dimensions, 51 × 51 × 51 mm; trapping voltage, +1.0–2.0 V; 32K data points; mass range, 26–400 amu; trapping times, 0–1000 ms; pressure of SiD_4, $(0.6\text{–}3.0) \times 10^{-6}$ Torr (uncorrected ion gauge reading); cell temperature, 25 °C. The isotopically labeled Si^+ (^{29}Si, *Si) was obtained by ejecting from the trapped ion cell the other silicon isotopes and silicon clusters present after laser ablation. All reaction pathways observed were verified by standard double resonance techniques;[12] elemental compositions of reactant and product ions were verified by accurate mass measurement to within 20 ppm. Note that there is insignificant ion loss from the trapped ion cell within 5 s of trapping time at the highest pressure examined.

Bimolecular reaction rate constants were determined for the majority of the cluster ions from the intensity decrease of the reactant ion as a function of time. Multiple measurements of selected rates at different pressures verified that the observed rate constants were linear in reactant pressure. Absolute rate constants reported were obtained by correcting the observed ion gauge reading both for the ionization cross section[13] and for the differential pressure between the ion gauge and the reaction cell which we determined kinetically.[14] The errors listed for the rate constants indicate their precision from multiple determinations; the accuracy, which is dependent upon the pressure correction scheme, is estimated to be ±50%. The measured reaction rates are scaled by the pressure correction scheme to obtain absolute rates. Thus the relative reaction rates are accurate to the error limits listed.

The kinetic analyses were complicated for some ions by the occurrence of nominally endothermic reactions due to the presence of excess energy. In these instances, the ions were allowed to "cool" by collision prior to kinetic analysis so that their ground-state reaction rates could be evaluated.

For $Si_3D_4^+$, determination of its reaction rate was complicated by its slow formation and subsequent rapid reaction with SiD_4. In this instance, the reaction rate was determined by using the steady-state approximation at the point where its intensity was balanced by its formation and decay.

Results and Discussion

Evidence for Structural Isomers. Since a mass spectrometer detects the mass-to-charge ratio of an ion, structural differences are not directly observed. Such differences may be observed by perturbing the ion, e.g., in some cases by collision-induced dissociation,[15] photodissociation,[16,17] or by monitoring ion/molecule chemistry.[18,19] For example, isomers of C_7^+ have been differentiated on the basis of their reactivity with D_2 and O_2.[19] We have employed the ion/molecule reaction technique to differentiate isomers of $Si_mD_n^+$ by observing the reaction products with SiD_4 of ions which have the same elemental composition but have been

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TABLE I: Identification of Structural Isomers and Excess Energy in Sequential Reactions of $Si_mH_n^+$ with SiD_4

reactant ion[a]	product ion[a,g]	form of reactant ion[b]	% abund[f]	reaction half-life (no. collisions)[c]	reaction rate[e]
$*Si^+$	$*Si_2D_2^+$	GS	90	1.5	6.9
$*Si_2D_2^+$	$*Si_3D_4^+$	isomer	100	29.0	0.32
$*Si_3D_4^+$	$*Si_4D_6^+$	isomer	100	4.8	1.7
$*Si^+$	$*SiD^+$	elec	10	1.5	8
$*SiD^+$	$*Si_2D^+$	vib	19	1.0	12[h]
$*SiD^+$	$*Si_2D_3^+$	GS	81	1.7	5.2
$*Si_2D^+$	$*Si_2D_2^+$	vib	100	3.2	3.1
$*Si_2D_2^+$	$*Si_2D_3^+$	isomer	(100)[d]	1.9	5
$^{28}Si^+$	$^{28}SiD^+$	kin			
$^{28}SiD^+$	$^{28}Si_2D_2^+$	elec + vib	17	5.0	3.3[h]
$^{28}SiD^+$	$^{28}Si_2D_3^+$	elec[i]	83	170[i]	0.09[i]
$Si_2D_2^+$	$Si_3D_4^+$	isomer	100	7.0	1.2
$Si_3D_4^+$	$Si_4D_4^+$	isomer	100	4.3	1.8
Si_2^+	Si_2D^+	vib	7	1.0	10[h]
Si_2^+	Si_3^+	vib	7	1.0	10[h]
Si_2^+	$Si_3D_2^+$	GS	86	4.0	2.5[h]
$Si_4D_2^+$	$Si_5D_4^+$	isomer	75	7.0	1.3
$Si_4D_2^+$	NR	isomer	25	≥9000	≤0.001

[a] *Si represents single ^{29}Si in ion from $^{29}Si^+$ reaction; NR = no reaction. [b] GS = ground state, isomer = structural isomer; vib = excess vibrational energy; elec = excess electronic energy; kin = excess kinetic energy. [c] Number of collisions (relative to the Langevin collision rate) required for the reactant population to be half-consumed. [d] Estimated to be the exclusive reaction pathway. Poor signal-to-noise prohibits certain determination. [e] Units of $cm^3/(molecule \cdot s) \times 10^{10}$. [f] Percent of reactant ion which forms specified product ion. [g] Excludes isotope exchange reaction. [h] Vibrationally excited ions could have a range of excess energy. It is conceivable that the amount of excess energy also affects the reaction rate, resulting in multiple exponential decays. This data was fit assuming a single exponential decay. [i] Since the product is identical with that of ground-state SiD^+, this reaction rate may represent the ion's radiative decay rate to the ground electronic state.

formed from different ions. The assignments of structural isomers and excess energy are summarized in Table I.

In some instances the evidence is straightforward; the isomeric species react with SiD_4 to form totally different products. For example, there are three parallel sets of reactions which produce distinct species of $Si_2D_2^+$ ($*Si_nD_m^+ = {}^{29}Si^{28}Si_{n-1}D_m^+$; $*Si^+\# =$ electronically excited Si^+):

$$*Si^+ \xrightarrow[-D_2]{SiD_4} \underset{\mathbf{1}}{*Si_2D_2^+} \xrightarrow[-D_2]{SiD_4} *Si_3D_4^+ \xrightarrow[-D_2]{SiD_4} *Si_4D_6^+ \qquad (1)$$

$$*Si^+\# \xrightarrow[-SiD_3]{SiD_4} *SiD^+ \xrightarrow[-2D_2]{SiD_4} *Si_2D^+ \xrightarrow[-SiD_3]{SiD_4} \underset{\mathbf{2}}{*Si_2D_2^+} \xrightarrow[-SiD_3]{SiD_4} *Si_2D_3^+ \qquad (2a)$$

$$\xrightarrow[-D_2]{} *Si_2D_3^+ \qquad (2b)$$

$$Si^+ \xrightarrow[-SiD_3]{SiD_4} SiD^+\# \xrightarrow[-D_2,\, D]{SiD_4} \underset{\mathbf{3}}{Si_2D_2^+} \xrightarrow[-D_2]{SiD_4} Si_3D_4^+ \xrightarrow[-2D_2]{SiD_4} Si_4D_4^+ \qquad (3)$$

The reaction of Si^+ to form $Si_2D_2^+$ (**1**), shown in reaction 1, has been determined to be the reaction of ground-state Si^+.[5,6,20] The first step in reaction 2 is endothermic by 17 kcal/mol,[20] so it must involve a higher energy form of Si^+ (this will be discussed later). Reaction 3 involves unlabeled SiD^+ which in our experiment must be derived from reaction of $^{28}Si^+$, kinetically excited during double resonance ejection, with $^{28}SiD_4$. The formation of SiD^+ showed a dramatic pressure dependence; it was not formed at 6×10^{-7} Torr whereas it was readily observed at 2×10^{-6} Torr. The reason is the length of time between collisions relative to the time required to be ejected from the cell. It is clear from the different reaction products that this SiD^+ differs from that formed in reaction 2 (vide infra). Also, the $Si_2D_2^+$ (**2**) formed in reaction 2 differs from the $Si_2D_2^+$ produced in either reaction 1 or 3 since it forms a different product, $Si_2D_3^+$, vs $Si_3D_4^+$. $Si_2D_2^+$ formed in reactions 1 and 3 both produce $Si_3D_4^+$, but these ions in turn react to form different products (either $*Si_4D_6^+$ or $Si_4D_4^+$), indicating that both $Si_2D_2^+$ and $Si_3D_4^+$ in reactions 1 and 3 are different species. Further evidence is obtained from the reaction rates as shown in Table I.

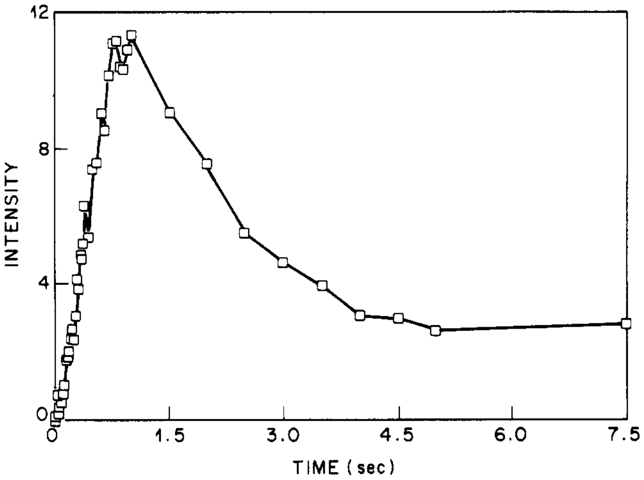

Figure 1. Plot of the normalized, isotope-corrected intensity of $Si_4D_2^+$ as a function of reaction time with 4×10^{-7} Torr of SiD_4. Note the nonreactive portion at greater than 5-s reaction time.

Another isomer set is observed for $Si_4D_2^+$. The differentiation is based upon the decay of the ion intensity when reacted with SiD_4 (Figure 1). Both isomers of $Si_4D_2^+$ are formed in the ground-state reaction of Si_3^+ with SiD_4. Note that only a portion of the $Si_4D_2^+$ ion population decays; thus there is one set, comprising 25% of the $Si_4D_2^+$ population, that does not react. This is viewed as the presence of two structural isomers in the ratio of 3:1.

$$Si_4D_2^+ + SiD_4 \rightarrow Si_5D_4^+ + D_2 \qquad (4)$$

$$Si_4D_2^+ + SiD_4 \rightarrow NR \qquad (5)$$

There is the possibility that the reactive population consists of ions with excess energy. This is discounted since $Si_4D_2^+$ is formed in the ground-state reaction of Si_3^+, the reactive portion represents the majority (75%) of the population, and the reaction rate is only about 10% of the collision rate. The presence of reactive and nonreactive isomers is analogous to the observed reactivity of two C_7^+ isomers with D_2.[19]

Excess Energy: *Vibrational vs Electronic*. Reaction of structural isomers can be contrasted with the reaction of ions that contain excess internal energy. Vibrational excitation can occur in these experiments either by formation of a vibrationally "hot" population from laser ablation or from interconversion of an electronically excited state (also formed during laser ablation) to a vibrationally excited ground state.[16] The latter situation can potentially produce far more excess energy in the ion than the former but would still exhibit the characteristics of vibrational excitation. Excess vibrational energy manifests itself by opening up endothermic ground-state reaction channels in competition with the exothermic reaction channels. Once the population of ions with excess vibrational energy is depleted (by complete reaction or through quenching of excess energy—vide infra), the endothermic reaction channels are closed. This is exemplified by the reaction of Si_2^+:

$$Si_2^+ + SiD_4 \rightarrow Si_3D_2^+ + D_2 \qquad (6)$$

$$\rightarrow Si_3^+ + 2D_2 \quad \text{(endothermic)} \qquad (7)$$

$$\rightarrow Si_2D^+ + SiD_3 \quad \text{(endothermic)} \qquad (8)$$

Figure 2 shows the time dependence for these ion intensities. The plot of the time dependence of the Si_2D^+ population has been excluded for clarity (its intensity/time plot nearly overlaps that

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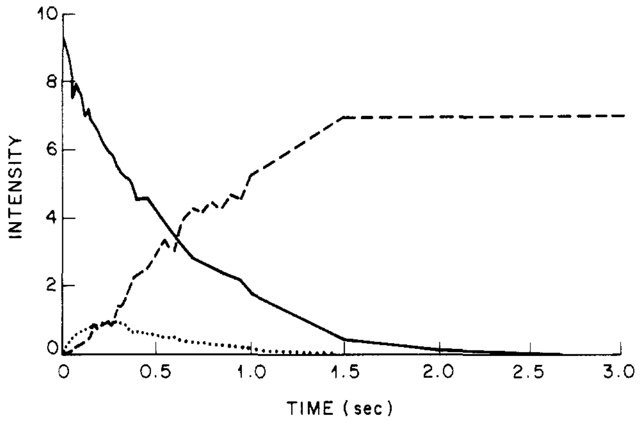

Figure 2. Normalized, isotopically corrected intensities of Si_2^+ (solid line) and two of its primary products, Si_3^+ (dotted line) and $Si_3D_2^+$ (dashed line), as a function of time. Note that the intensity of Si_3^+ decreases at an early time. This is due to its formation from vibrationally excited Si_2^+ which is quenched or fully reacted within 300 ms. Another reaction product of vibrationally excited Si_2^+, Si_2D^+, is not plotted since its intensity nearly overlaps that of Si_3^+.

of Si_3^+). Note that formation of Si_3^+ and $Si_3D_2^+$ compete at early times (<500 ms) but at later times formation of Si_3^+ has ceased; Si_3^+ reacts away in the same time frame as Si_2^+. Double resonance[12] confirms the accuracy of reactions 6–8; the explanation is that a portion of the Si_2^+ population has excess energy.

The possibility of structural isomeric species for Si_2^+ is discounted (this explanation is not possible for Si_2^+ but is relevant to other systems). It is assumed that isomers will react to form different unique products. This is observed for the isomers of $Si_2D_2^+$. When one of the species forms all of the products that the ground-state species does plus one or more other products, the simplest explanation is to assign the presence of excess vibrational (or kinetic) energy to the latter species.

The $Si_3D_2^+$ time-dependent intensity indicates that it is not formed from a single population (the ground state) of Si_2^+. The temporal variation of its intensity does not simply follow eq 9.

$$I = I_0\,(1 - e^{-k}t) \qquad (9)$$

Figure 3A compares the intensity rise of $Si_3D_2^+$ with the expected curve shape. The measured reaction rate constant, k, was used to evaluate eq 9. The curve shows deviation from the smooth curve at short times where it should correlate with the exponential decay of Si_2^+. Figure 3B compares this expected curve with the combined intensities of $Si_3D_2^+$, Si_3^+, and Si_2D^+. This latter figure shows excellent agreement indicating that formation of $Si_3D_2^+$ was suppressed by the opening up of these normally endothermic reaction channels. Thus $Si_3D_2^+$ is produced from all forms of Si_2^+. The simplest explanation is the presence of excess vibrational energy in a portion of the population.

An important reaction of silicon clusters with SiD_4 that involves excess vibrational energy is the opening up of a reaction channel where a second molecule of D_2 is lost (e.g., reaction 7). This can be envisioned as sequential processes where a portion of the initial product ($Si_3D_2^{+\#}$) retains sufficient excess energy to lose another molecule of D_2:

$$Si_2^+ + SiD_4 \rightarrow D_2 + [Si_3D_2^{+\#}] \rightarrow D_2 + Si_3^+ \qquad (10)$$

The second loss of D_2 can be facile. This is exemplified by the ease with which $Si_3D_2^+$ forms Si_3^+ during ion ejection. In attempting to remove $Si_3D_2^+$ from the cell (double-resonance ejection[12]), Si_3^+ was formed efficiently by collision of the kinetically excited $Si_3D_2^+$ with SiD_4. This was an unintentional collision-induced dissociation (CID) experiment.[21] $Si_3D_2^+$ was the most easily dissociated ion encountered in all of our experiments. This points out a caution: double resonance can produce artifacts due to the CID process.

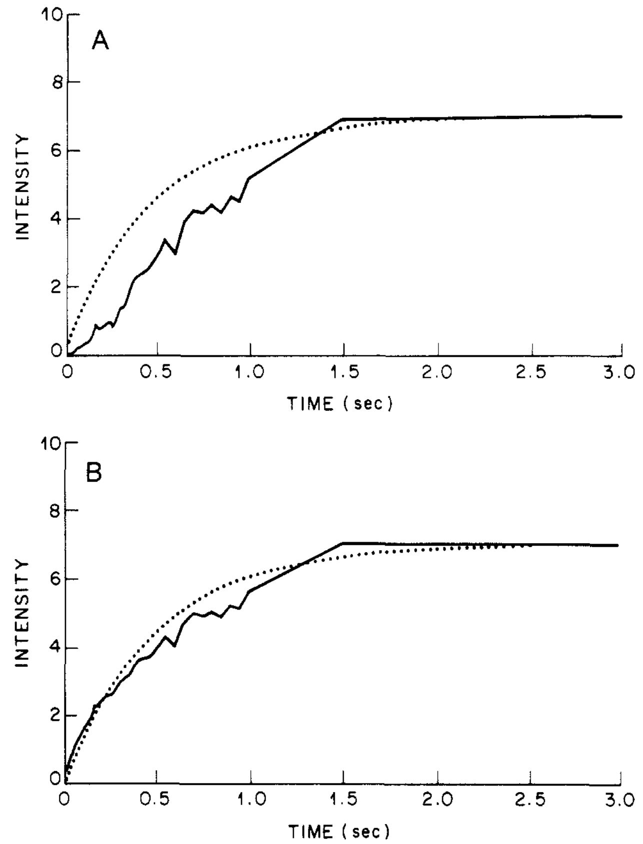

Figure 3. Comparison of the growth in intensity of Si_2^+ products and the expected growth curve from eq 9 (dotted line). (A) The $Si_3D_2^+$ intensity (solid line) is shown for comparison. The deviation from the expected curve illustrates that a portion of the products have not been accounted for. The normally endothermic reaction channels which form Si_2D^+ and Si_3^+ open up due to the presence of vibrationally excited Si_2^+ and result in a decrease in the probability of forming $Si_3D_2^+$. (B) Plot for the combined intensities for all Si_2^+ reaction products with SiD_4: Si_2D^+, Si_3^+, and $Si_3D_2^+$ (solid line). The curve compares favorably with the expected curve from eq 9, demonstrating that only one Si_2^+ species is present.

Another caution in the use of double resonance is when excess kinetic energy is provided which can open up a new reaction channel. This is evident for Si^+ to form SiD^+ (reaction 3). Kinetically excited ions can carry >10 eV of translational energy.[22] As for vibrationally excited ions, this energy can open up endothermic reaction channels in competition with the normal exothermic channels. On the other hand, electronically excited Si^+ forms a different species in reaction 2 (vide infra).

Ascribing those processes that result from excess electronic energy can be more difficult to identify. The least ambiguous indications of its presence have been made for atomic[23,24] or diatomic ions[25] with no possible structural isomers but with the possibility of long-lived electronic states. Larger ions often interconvert quickly from an excited electronic state to vibrationally excited ground electronic states.[16] The argument for differentiating species with excess vibrational (or kinetic) energy from species with excess electronic energy is the same as for differentiating species with excess vibrational energy from isomeric species: the electronically excited species must react to form products that are unique. Differentiating electronically excited species from isomeric species is done simply on the basis of size: an atomic or diatomic species cannot have isomeric forms, so when the above criteria are met, the species are assumed to be in an electronically

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excited state. Under the same circumstances triatomic or larger species are assigned isomeric forms. These are the assumptions used in evaluating the data in this work. The only exception is the evaluation of Si^+ in reaction 3. The reaction is ascribed to a kinetically excited species; it does not follow the above criteria. At present we are unable to offer an alternative explanation.

For Si^+, the formation of SiD^+ from SiD_4 in reaction 2 is 17 kcal/mol endothermic.[20] An excited electronic state of Si^+ with a forbidden transition to the ground state must be invoked. One long-lived excited state is known (^4P) with an energy of 5.3 eV and a lifetime of ~5 s. It is interesting that the reaction of kinetically excited Si^+ (reaction 3) and electronically excited Si^+ (reaction 2) both produce SiD^+, but in different forms. In fact, it appears that electronically excited Si^+ forms SiD^+ in its ground electronic state (with some excess vibrational energy) (reaction 2) whereas kinetically excited Si^+ forms SiD^+ in its excited electronic state (reaction 3).

In the case of SiD^+ in reactions 2 and 3, exclusive formation of different products shows that this is not simply an instance of excess vibrational energy. Prior studies on the ion/molecule chemistry of $SiH_n{}^+$ with SiH_4 found SiH^+ to react exothermically with SiH_4. Recent results show that formation of Si_2H^+ from SiH^+ is endothermic by 23 kcal/mol whereas formation of $Si_2D_3{}^+$ is exothermic by 16 kcal/mol.[20] This is in agreement with our results, which show formation of Si_2D^+ ceases while $Si_2D_3{}^+$ continues to be formed in reaction 2 (cf. Table I). Since formation of Si_2D^+ initially parallels formation of $Si_2D_3{}^+$, it must occur from vibrationally excited states which react rapidly in preference to being quenched. The second step of reaction 3 to form $Si_2D_2{}^+$, which is endothermic by 39 kcal/mol,[20] must occur, through an excited electronic state of SiD^+. One excited state ($^1\Pi$), with an energy of 3.2 eV, has been well characterized both spectroscopically[26] and theoretically.[27,28] However, this state is probably short-lived and, therefore, would not survive on the time frame of our experiments (1–100 ms). Another state ($^3\Pi$) has been calculated[27,28] and recently observed.[29] This state could be sufficiently long-lived so as to react on our experimental time scale. The portion of the SiD^+'s population that slowly reacts (cf. Table I) cannot be ascribed to the ground state (vide supra). We suggest that formation of $Si_2D_2{}^+$ comes from a vibrationally excited electronic state SiD^+ whereas the slowly reacting portion is electronically excited SiD^+ with no excess vibrational energy. The observed slow reaction rate of SiD^+ could be due to a symmetry-forbidden reaction. Alternatively, the slow reaction rate could correspond to either the collision quenching rate or the radiative emission rate for the triplet state with a subsequent fast reaction of the newly formed ground state SiD^+. This latter possibility would also require that reaction 3 for $SiD^+(^3\Pi)$ is forbidden in its lowest vibrational state and that the lifetime for this state is approximately 3 s. The reaction product corresponds to that of ground-state SiD^+, $Si_2D_3{}^+$.

Quenching of Excess Energy. It is obvious that excess energy is present in some of the $Si_mD_n{}^+$ ions. Quenching the excess vibrational or electronic energy by a nonreactive collision with a neutral would be useful to distinguish it from the reactions of structural isomers (radiative loss of the energy[30] is possible but was only considered for SiD^+). How difficult is it to quench the excess energy, and is this quenching dependent upon the form it takes? A summary of our conclusions is presented in Table I. Quenching of excess vibrational energy usually requires removal of several quanta of energy; this will typically occur in multiple collisions. We have found that four to seven collisions with SiD_4 are required to deplete the population which contains excess vibrational energy. During this time there is competition between reaction and quenching. In some instances, the quenching and/or reaction can occur in a single collision (e.g., SiD^+ and $Si_2{}^+$). This is true when the ground state is extremely reactive (four to seven collisions for reaction). The reaction of a vibrationally "hot" ion would normally be expected to occur in fewer collisions. In these instances, quenching by SiD_4 has a low probability; i.e., essentially all of the excited reactants react rather than be quenched.

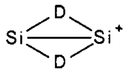
For electronic excitation, there is significantly more energy as compared with vibrational excitation, so the reactions, if allowed, occur more efficiently as well. For Si^+, the excited-state reaction is quite efficient; its reaction (or quenching) occurs in a single collision. On the other hand, even though it has sufficient energy to form normally endothermic products, electronically excited $SiD^+(^3\Pi)$ reacts slowly. (We cannot distinguish between slow reaction and quenching followed by fast reaction of the ground state.) Even collisional quenching is inefficient, taking ≥170 collisions.

Structural isomers can often interconvert, leading ultimately to the lowest energy isomer. For $Si_2D_2{}^+$, $Si_3D_4{}^+$, and $Si_4D_2{}^+$ this is clearly not the case. Their identity is retained through several reaction steps involving more than 50 collisions. Such stability indicates high barriers to interconversion.

Isomer Structures. Ab initio electronic structure calculations have been invaluable toward understanding the noninterconversion of the $Si_2D_2{}^+$ isomers. The ground-state reaction of $^*Si^+$ has been examined experimentally and theoretically[9,31] and has been shown to yield an $Si_2D_2{}^+$ isomer which does not have the lowest energy geometry:

$$^*Si^+(^2P) + SiD_4 \rightarrow \underset{\mathbf{1}}{D_2Si{-}^*Si^+} + D_2 \qquad (11)$$

The lowest energy $Si_2D_2{}^+$ isomer has a doubly bridged, nonplanar structure, **2**[31]



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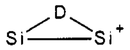
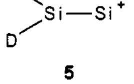
which corresponds to the lowest energy structure for the neutral.[32,33] The barrier to interconversion of isomeric structure **2** to **1** is calculated to be 17 kcal/mol.[31] Furthermore, there is a barrier in the mechanism of reaction 11 that prevents ground-state Si^+ from directly forming **2**.

The most stable isomer, **2**, is only observed to be formed by deuterium transfer to Si_2D^+ in reaction 2. A factor which may be important to achieving this structure is that it is formed from Si_2D^+, which probably has the unique structure[31]

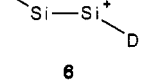


4

Subsequent addition of a deuterium atom to **4** should yield the most stable isomer, **2**. Note that this is calculated to be endothermic and therefore must occur from an excited state. The final $Si_2D_2{}^+$ structure (**3**) formed in reaction 3 is less certain. Ab initio calculations[31] show the presence of two quartet forms corresponding to **5** and **6** with the former being slightly more stable



5



6

and both lying 35–40 kcal/mol above the lowest energy isomer **2**. By inference, we postulate one of the quartets to be the structure formed in reaction 3.

The presence of isomers complicates the experimental determination of reaction rates and thermochemistries. The heat of formation of $Si_2H_2{}^+$, derived from electron impact on Si_2H_6, has

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been reported to be 290,[34] 286,[35] and 264–290[5] kcal/mol whereas the heat of formation of $Si_2D_2^+$ derived from reaction 1 has been found to be <268 kcal/mol.[20] The reaction rate of $Si_2H_2^+$, derived from electron impact on Si_2H_6, with SiH_4 relative to the reaction rate of Si_2^+ with SiH_4 has been found to be 0.22.[6] We have found this relative reaction rate to be 0.12, 0.48, and 2.0 for $Si_2D_2^+$ structures **1**, **5** or **6**, and **2**, respectively. It is apparent that $Si_2H_2^+$ derived from electron impact on Si_2H_6 does not necessarily correspond to the same structure as that formed in the ground-state reaction of Si^+.

Implications for Silane Plasma Reactions. The environment within a plasma reactor is extremely complex. Temperature and pressure gradients occur as well as localized concentrations of ions. Heating is accomplished primarily by impact of electrons accelerated with the rf or dc field. Such a process can readily produce ions with excess vibrational energy and even electronically excited species. As shown above, the internal energy content can alter the reaction rate. If ions such as Si^+ or SiH^+ are produced in electronically excited states, then they will follow reaction sequences that differ from the reaction sequences of the ground-state species. Excess vibrational or kinetic energy can open up nominally endothermic reaction channels, e.g., reactions 7 and 8. The facile loss of molecular hydrogen, as in reaction 10, may be an important mechanism in the plasma for reducing the hydrogen content of larger gas-phase silicon ions. Corresponding processes for the neutral species are quite likely but have not been investigated. Finally, the reaction rates for bare and hydrogenated silicon cluster ions are not constant, as silane plasma models presume,[1-4] and also depend upon the isomer formed.

Implications for Cluster Chemistry. When the chemistry of a group of clusters is examined, the reactions are assumed to be from the ground state of the cluster. A portion of the silicon clusters formed by laser ablation do have some excess energy that allows formation of normally endothermic products. Prior studies gave only slight indications for the presence of excess energy.[11,36-39] In our study the reactivity for clusters with excess vibrational energy was found to be enhanced. This observation was made by taking advantage of the low reactant pressure which allowed for a detailed study of the time dependence of the reaction kinetics. For reaction studies that simply examine initial and final ion intensities, the misassignment of endothermic reaction channels as exothermic channels is possible as in the case of SiH^+.[40]

Summary

Noninterconverting structural isomers are observed for $Si_2D_2^+$, $Si_3D_4^+$, and $Si_4D_2^+$; the structure present is dependent upon how the ions are formed. The isomers have reaction rates with SiD_4 which vary significantly, and in addition, each isomer forms a unique reaction product.

The presence of excess energy is also evident for some of the reactant ions. The excess energy may take the form of vibrational or electronic energy. Excess electronic energy is assigned to some atomic Si^+ and diatomic SiD^+ reactants. For the larger ions with excess energy, it is assumed to be present as vibrational energy since internal conversion of electronic to vibrational energy is expected to be fast on the time scale of these experiments. The quenching of excess vibrational and electronic (for Si^+) energy competes with reaction, so the quenching probabilities with SiD_4 are difficult to ascertain. For $SiD^+(^3\Pi)$ in the vibrational ground state, reaction is very slow. Therefore, $SiD^+(^3\Pi)$ appears to be an unreactive species that is inefficiently quenched and/or has a slow radiative decay. The observed slow reaction may either derive from a fast reaction of the slowly formed ground electronic state of SiD^+ or a slow reaction of the excited state.

The presence of multiple isomers with differing reaction rates and products have not been included in models of silane plasma reactors. The chemistry within the reactors is further complicated by the presence of vibrationally and electronically excited species which undergo normally endothermic reactions at reaction rates greater than those for the competing ground-state species. Finally, near-thermoneutral elimination of hydrogen from partially hydrogenated silicon cluster ions is observed for $Si_3D_2^+$ and may be a common reaction even for neutral species.

Registry No. SiD_4, 13537-07-0; $^*Si^+$, 51377-76-5; $^*SiD^+$, 113687-06-2; $^*Si_2D^+$, 113687-07-3; $^*Si_2D_2$ (isomer I), 113687-08-4; $^*Si_2D_2$ (isomer II), 113687-09-5; Si_2, 12597-36-3; ^{28}Si, 14276-58-5.

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