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REACTION OF ANIONIC AND CATIONIC SILICON CLUSTERS WITH TUNGSTEN HEXAFLUORIDE STUDIED BY FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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Anionic and cationic silicon clusters react exothermically with WF_6 to give a variety of tungsten and silicon fluorides. All the silicon anionic clusters transfer their charge to WF_6. The electron affinities of Si_{2-6} are estimated to be less than the electron affinity of WF_6 (350 kJ/mole (3.6 eV)).

1. Introduction

The availability of techniques for generating clusters has made it possible to study cluster chemistry and gain an understanding of how it changes as a function of cluster size or charge. Particularly interesting should be comparisons of cluster properties and reactions with those of the "bulk" material [1–3]. At what size does a cluster exhibit the chemistry of the bulk? An examination of the reaction products of small clusters may provide insights into their chemistry and may eventually lead to an understanding at the microscopic level of chemical reactions occurring on surfaces.

We have previously examined the growth of silicon clusters by bimolecular reactions with methylsilane [1]. In this paper we examine the fluorination of anionic and cationic silicon clusters containing up to six atoms by bimolecular reactions with tungsten hexafluoride in the ion trap of a Fourier transform mass spectrometer. Tungsten hexafluoride is known to react with bulk silicon to both etch the silicon by fluorine transfer and deposit metallic tungsten [4]. We chose to examine this system to determine if any parallel reactions would occur for small silicon clusters, perhaps even to shed light onto details of the tungsten deposition process. We find that the smaller clusters (<4 atoms) exhibit a multitude of reaction products. For the larger clusters, monofluorination and, for the anionic clusters, charge transfer dominate. From the observed product distributions and reaction rates, both available reaction sites on the clusters (the radical center and silylene groups) participate in the reactions. These cluster reactions provide an insight into tungsten deposition onto bulk silicon.

2. Experimental

A pulsed Nd:YAG laser (typical powers 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 07820) just outside of the trapping call of a modified Nicolet FT/MS-1000 Fourier transform mass spectrometer. 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 × 101 mm; trapping voltage, +0.6 V for Si_n^+ and −0.6 V for Si_n^-; 32K data points; mass range, 26–400 amu; trapping times, 0–1000 ms; pressure of WF_6, $(0.6\text{–}3.0)\times10^{-6}$ Torr (uncorrected ion gauge reading); cell temperature, 25 °C. All reaction pathways observed were verified by standard double resonance techniques [5]; elemental compositions of reactant and product ions were verified by accurate mass measurement to within 20 ppm.

Bimolecular reaction rate constants were determined from the intensity decrease of the reactant ion as a function of time. Multiple measurements 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 for the ionization cross section [1,6], derived from the molecular polarizability of WF_6 [‡], and a differential pressure between the ion gauge and the cell determined kinetically [9]. 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 pressure correction adjusts the ion gauge reading to give a more accurate absolute pressure. This results in increasing or decreasing all rate constants equally and does not affect their relative values.

With the low laser power density used, formation of multiply charged silicon clusters are not observed although they have been observed under higher power ablation conditions. Multiply charged silicon clusters can be differentiated in a Fourier transform mass spectrometer (FTMS) by observing the isotopic pattern of the cluster; their ^{29}Si isotope would appear at non-integer masses. This will differentiate even those multiply charged clusters whose masses would overlap the masses of a smaller cluster.

3. Results and discussion

Laser-generated ionic silicon clusters [10] were trapped in an FTMS in order to study their reaction kinetics and product distributions. The initial distribution of cationic and anionic cluster ions have been described previously [1]. After introduction of tungsten hexafluoride into the mass spectrometer, the silicon clusters were observed to undergo exothermic, bimolecular reactions. Reactant and product ions are detected with equal efficiency.

3.1. Reaction kinetics

The time dependences of the ion intensities were examined to obtain kinetic data. The reactions can be described by pseudo-first-order rate constants which are proportional to WF_6 pressure. The rate constants for these reactions are presented in tables 1 and 2.

The cationic silicon clusters exhibit a smooth decrease in reaction rate from Si^+ to Si_3^+. Between Si_3^+ and Si_4^+ there is a precipitous decrease in reaction rate; the reaction rate then remains relatively constant for larger clusters. This contrasts with the reaction rates with methylsilane; the overall decrease continued to Si_5^+ after which the precipitous drop in reaction rate (greater than an order of magnitude) occurred [1]. The absolute rates are close to the Langevin collision rate for Si_2^+ and Si_3^+. For Si^+, the measured reaction rate exceeds the Langevin collision rate by a factor of two. This is due both to the simplicity of the Langevin equation, which can underestimate the reaction rate, and the uncertainty in the correction factors (±50%).

The anionic silicon clusters exhibit little variation in overall reaction rate in contrast to the cationic clusters; this results from the dominance of charge transfer. However, several other processes are competitive with this reaction channel (table 2). The reaction rate constants for the anions are greater than the Langevin collision rate, possibly indicating a long range charge transfer.

3.2. Reaction products and thermochemistry

The product distributions as a function of cluster size and charge are shown in tables 1 and 2. For the anions, charge transfer to WF_6 is dominant but other reaction pathways compete successfully. The driving force in all of these reactions is formation of strong silicon–fluorine bonds (BE ≈ 600 kJ/mole) at the expense of weaker tungsten–fluorine bonds (BE ≈ 500 kJ/mole). This energy difference has a significant influence on the reaction mechanism. A dominant feature of the reactions appears to be the production of the stable neutral SiF_2 resulting from, for example, ionic Si to form ionic WF_4, ionic Si_2 to form ionic WF_2, and ionic Si_3 to form $WSiF_2$. This correlates with the observation that SiF_2 is a primary species evolved during fluorine etching of a silicon surface [11]. Note that many products are the same regardless of whether an anion or a cation was the reactant.

Several features are noteworthy. First, in some

[‡] Value calculated from the equation in ref. [7] and molecular polarizability of $W(CO)_6$ from ref. [8].

Table 1
Reaction of cationic silicon clusters with WF_6

Reaction [a]			Product fraction (%)	Rate constant [b] (10^{-10} cm^3/molecule s)
$Si^+ + WF_6 \rightarrow$	SiF^+	$+ WF_5$	14	39 ± 10
	WF_3^+	$+ SiF_3$	1	
	WF_4^+	$+ SiF_2$	67	
	WF_5^+	$+ SiF$	18	
$Si_2^+ + WF_6 \rightarrow$	SiF^+	$+ WF_3 + SiF_2$	7	13 ± 4
	Si_2F^+	$+ WF_5$	8	
	$Si_2F_2^+$	$+ WF_4$	8	
	WF_2^+	$+ 2SiF_2$	27	
	WF_3^+	$+ SiF_2 + SiF$	15	
	WF_4^+	$+ Si_2F_2$	22	
	WF_5^+	$+ Si_2F$	13	
$Si_3^+ + WF_6 \rightarrow$	Si_3F^+	$+ WF_5$	7	9.6 ± 2
	$Si_3F_2^+$	$+ WF_4$	4	
	WF_2^+	$+ SiF_2 + Si_2F_2$	2	
	WF_3^+	$+ SiF_2 + Si_2F$	5	
	WF_4^+	$+ Si_3F_2$	17	
	$WSiF_2^+$	$+ 2SiF_2$	55	
	$WSiF_3^+$	$+ SiF_2 + SiF$	5	
	$WSiF_4^+$	$+ Si_2F_2$	5	
$Si_4^+ + WF_6 \rightarrow$	Si_4F^+	$+ WF_5$	100	0.51 ± 0.13
$Si_5^+ + WF_6 \rightarrow$	Si_5F^+	$+ WF_5$	100	0.25 ± 0.03
$Si_6^+ + WF_6 \rightarrow$	Si_6F^+	$+ WF_5$	100	0.41 ± 0.3

[a] Most thermodynamically stable neutral products are listed.

[b] Uncertainties reflect the precision of multiple measurements which are, for example, affected by relative strengths of initial cluster ion signals.

reaction channels, ions for both of the products are present (all thermochemical calculations are based upon the values presented in table 1):

$$Si^+ + WF_6 \rightarrow SiF^+ + WF_5$$

$$\Delta H_{rxn} = -99 \text{ kJ/mole}, \qquad (1)$$

$$Si^+ + WF_6 \rightarrow WF_5^+ + SiF$$

$$\Delta H_{rxn} = 164 \text{ kJ/mole}. \qquad (2)$$

This unusual occurrence must result from both reaction pathways being exothermic. Unfortunately, the thermochemistry of the tungsten subfluorides is not well known; the available information may be incorrect. For example, consider the reaction of Si^+ with WF_6 resulting in fluorine transfer (reactions (1) and (2)). Based on the literature data reaction (2) is significantly endothermic. In spite of this apparent endothermicity, both reactions (1) and (2) are observed to be significant exothermic pathways [#]. It appears that the thermochemical data for WF_5/WF_5^+ (cf. table 3) are in error; the ΔH_f of WF_5, its ionization potential or both are too positive. When, on the other hand, these reactions are considered,

$$Si^+ + WF_6 \nrightarrow SiF_2^+ + WF_4$$

$$\Delta H_{rxn} = 35 \text{ kJ/mole}, \qquad (3)$$

$$Si^+ + WF_6 \rightarrow WF_4^+ + SiF_2$$

$$\Delta H_{rxn} = -101 \text{ kJ/mole}, \qquad (4)$$

[#] The possibility of excess energy in the ions (either electronic or kinetic) has been discounted. See ref. [1].

Table 2
Reactions of anionic silicon clusters with WF_6

Reaction [a]			Product fraction (%)		Rate constant [b] (10^{-10} cm^3/molecule s)
			with WF_6^-	excl. WF_6^-	
$Si^- + WF_6 \rightarrow$	SiF^-	$+ WF_5$	2	15	25 ± 7
	WF_4^-	$+ SiF_2$	3	19	
	WF_5^-	$+ SiF$	9	67	
	WF_6^-	$+ Si$	86		
$Si_2^- + WF_6 \rightarrow$	$Si_2F_2^-$	$+ WF_4$	0.4	2	66 ± 17
	SiF_3^-	$+ WF_2 + SiF$	0.1	1	
	WF_2^-	$+ 2SiF_2$	16	77	
	WF_3^-	$+ SiF_2 + SiF$	0.4	2	
	WF_4^-	$+ Si_2F_2$	2	9	
	WF_5^-	$+ Si_2F$	2	10	
	WF_6^-	$+ Si_2$	79		
$Si_3^- + WF_6 \rightarrow$	$Si_3F_2^-$	$+ WF_4$	0.1	2	40 ± 12
	WF_2^-	$+ SiF_2 + Si_2F_2$	2	40	
	$WSiF_2^-$	$+ 2SiF_2$	3	58	
	WF_6^-	$+ Si_3$	94		
$Si_4^- + WF_6 \rightarrow$	Si_4F^-	$+ WF_5$	0.2	3	33 ± 2
	$WSi_2F_2^-$	$+ 2SiF_2$	2	30	
	WF_2^-	$+ SiF_2 + Si_3F_2$	2	34	
	WF_5^-	$+ Si_4F$	2	34	
	WF_6^-	$+ Si_4$	94		
$Si_5^- + WF_6 \rightarrow$	Si_5F^-	$+ WF_5$	6	38	26 ± 7
	$WSi_3F_2^-$	$+ 2SiF_2$	10	62	
	WF_6^-	$+ Si_5$	84		
$Si_6^- + WF_6 \rightarrow$	WF_5^-	$+ Si_6F$	2	100	37 ± 22
	WF_6^-	$+ Si_6$	98		

[a] Most thermodynamically stable neutral products are listed.

[b] Uncertainties reflect the precision of multiple measurements which are, for example, affected by relative strengths of initial cluster ion signals.

$$Si^+ + WF_6 \rightarrow WF_3^+ + SiF_3$$

$$\Delta H_{rxn} = -30 \text{ kJ/mole}\,, \qquad (5)$$

$$Si^+ + WF_6 \not\rightarrow SiF_3^+ + WF_3$$

$$\Delta H_{rxn} = -42 \text{ kJ/mole}\,, \qquad (6)$$

the observed reactions (4) and (5) are basically consistent with the known thermochemistry. Formation of SiF_2^+ (reaction (3)) is endothermic by only 35 kJ/mole and is not observed. The thermochemical data for WF_4 are consistent with the observed reactions. Note, however, that both reaction (1) and reaction (4) are exothermic by roughly 100 kJ/mole, yet reaction (4) occurs four times more frequently. As pointed out, the thermochemistry of the tungsten subfluorides is not well known. In addition, the product distribution depends upon the intimate dynamics of the reaction and its inherent barriers to various reaction channels. For example, Si^+ may associate with two fluorines on WF_6 rather than one. This could result in favoring a simultaneous two flu-

Table 3
Relevant thermodynamic values

Species	H_f (kJ/mole)	EA (eV)	IP (eV)
Si	$456^{a)}$	$1.4^{f)}$	$8.21^{a)}$
Si_2	$594^{a)}$		
Si_3	$615^{a)}$		
SiF	$7^{a)}$		$7.3^{b)}$
SiF_2	$-619^{a)}$		$11.29^{b)}$
SiF_3	$-1051^{b,c,j)}$		$8.50^{b)}$
SiF_4	$-1615^{a)}$		$15.7^{b)}$
WF	$410^{c)}$		$8.5^{d)}$
WF_2	$-86^{d)}$		$9.0^{d)}$
WF_3	$-507^{d)}$		$9.0^{d)}$
WF_4	$-960^{d,e)}$	$2.6^{g)}$	$9.89^{d)}$
WF_5	$-1293^{d)}$	$1.2^{g,h,j)}$	$10.03^{d)}$
WF_6	$-1722^{a)}$	$3.6^{h,i,j)}$	–

a) Ref. [12]. b) Ref. [13]. c) Ref. [14].
d) Ref. [15]. e) Ref. [16]. f) Ref. [17].
g) Ref. [18]. h) Ref. [19]. i) Ref. [20].
j) Average of the two values referenced.

orine atom transfer rather than only a single atom transfer. Thermodynamic calculations are insufficient to answer this question. Note also that formation of both WF_3^+ and SiF_3^+ are exothermic, WF_3^+ is formed exclusively in spite of having a reported IP 0.5 eV higher than SiF_3^+.

Second, the thermochemistry (cf. table 3) for the reactions of Si^- is consistent with the observed reactions:

$$Si^- + WF_6 \rightarrow WF_4^- + SiF_2 \qquad \Delta H_{rxn} = -88 \text{ kJ/mole}, \tag{7}$$

$$Si^- + WF_6 \rightarrow WF_5^- + SiF \qquad \Delta H_{rxn} = -2 \text{ kJ/mole}, \tag{8}$$

$$Si^- + WF_6 \rightarrow SiF^- + WF_5 \qquad \Delta H_{rxn} < 0 \text{ kJ/mole}. \tag{9}$$

For reaction (9) the ΔH_{rxn} cannot be calculated due to an unknown electron affinity for SiF. Since the reaction is observed to be exothermic, an EA(SiF) > 110 kJ/mole (1.1 eV) is estimated.

Third, the larger cationic clusters, Si_4^+–Si_6^+, exhibit fewer products than do the smaller clusters; monofluorinated silicon clusters are observed exclusively. This change in the product distribution correlates with a sudden decrease in reaction rate with WF_6 between Si_3^+ and Si_4^+. A large distribution of products is observed for Si_{1-3}^+, whereas Si_nF^+ is the only product for the larger clusters. The majority of products present for the smaller clusters, excluding charge transfer for the anions, relies on multiple fluorination. The transfer of more than one fluorine to the larger clusters is either inhibited by a reaction barrier or the reaction exothermicity is so great that the intermediate dissociates to products before further fluorination can occur.

Fourth, the anions do exhibit charge transfer to WF_6. Of these silicon anions, only atomic silicon has a known electron affinity (133 kJ/mole (1.38 eV) [17]). Thus, upper limits to the electron affinities of Si_{2-7}^- are determined (EA < 350 kJ/mole (3.6 eV) [†]). Further bracketing experiments are underway to better determine these electron affinities.

Fifth, a monofluoride cluster anion is not formed except in the case of Si_5F^-. This does not necessarily mean that monofluorination does not occur if for the other negative clusters, WF_5 retains the charge. This would mean that Si_5F has an electron affinity significantly larger than WF_5 (120 kJ/mole (1.2 eV)) and the other silicon monofluoride clusters.

Sixth, many products are the same regardless of whether the reactant cluster is positively or negatively charged. This indicates that some common features are present for the two reaction mechanisms. The large difference in bond energy of a silicon–fluorine bond over a tungsten–fluorine bond is probably the reason.

Finally, formation of a silicon–tungsten bond is apparent for Si_3^+ and for Si_{3-5}^-. Since only select clusters form a tungsten–silicon bond, it is evidently not a prerequisite for reaction.

3.3. Reaction mechanism

3.3.1. Cations

Initial association would be from the cluster radical cation site to a fluorine on WF_6 to form a fluorine-bridged intermediate. Two reactive sites on the silicon cationic clusters must be considered: a radical ion and a silylene (lone pair electron) group [††] [21].

[†] Average of refs. [19,20].

[††] For a discussion on the reactions of silicon clusters with these groups, see ref. [1].

The subsequent chemistry of the two reactive sites with tungsten hexafluoride should differ. The radical would exhibit fluorine/fluoride abstraction [22], whereas a silylene group would insert into the tungsten–fluorine bond [23]. The Si_nF^+ products we observe (table 1) show definite signs of radical reaction. Formation of $WSiF_x^+$ most likely occurs via silylene insertion into a tungsten–fluorine bond. The remaining ionic products observed, e.g. WF_x, where $x=2$–4, results from multiple fluorine transfers to the silicon cluster. The reaction pathways other than monofluorination which involve neighboring silicon atoms shut down at Si_4^+. One may speculate that it is due to the stability of the closed structures for Si_{4-6}^+. Calculated structures indicate that ring opening for Si_3 is endothermic by only 8 kcal/mole with no barrier [24]. The resulting opened structure would have additional radical sites for fluorine to occur *. Larger clusters, which have highly unfavorable ring-opened structures (> 130 kcal/mole), [25] would not open to create a second radical site and therefore would be unable to transfer additional fluorines **. This is supported by the reactions of Si_5^- (vide infra) which exhibit silylene (insertion) behavior without undergoing multiple fluorinations. Further, endothermic ring opening would increase the lifetime of the complex by tying up some of the energy required to dissociate back to reactants. This would increase the opportunity for reaction before dissociation and result in more reactions per collision which is observed for the smaller cationic clusters.

3.3.2. *Anions*

A similar mechanism would be expected for the anionic clusters. Bonding of the cluster anion would occur at the radical anion site, through a bridging fluorine, to WF_6. Direct bonding of the silicon anion to the tungsten center of WF_6 to form a heptacoordinate tungsten intermediate is unlikely; this would require considerable reorganization of the tungsten's coordination sphere and therefore is expected to be slow. Electron transfer reactions of some organometallic compounds which require reorganization to accommodate the extra electron have been observed to be slow ($\approx 10\%$ of the collision rate) [26]. The observed reaction rates for the anionic silicon clusters in this study are, in fact, greater than the Langevin rate.

Note that Si_4^- and Si_5^- react to form a greater variety of products than their cation counterparts. One possible explanation is that Si_4^-, which undergoes both multiple fluorination and tungsten–silicon bond formation, may either exist as an open structure or else have a barrier to opening the ring that is far lower than for Si_4^+. Si_5^- exhibits monofluoride transfer in addition to insertion into the tungsten–fluorine bond (to form $WSi_3F_2^-$). Since silylene behavior (insertion into a tungsten–fluorine bond with formation of a tungsten–silicon bond) is observed for Si_5^- without the occurrence of multiple fluorination, we contend that multiple fluorinations occur through involvement of additional radical sites rather than involvement of silylene groups.

These mechanisms differ from the one used to explain the positive silicon cluster ion reactions with methylsilane [1]. In the latter case only silylene-type behaviour was observed, i.e. insertion into silicon–hydrogen bonds by divalent silicon centers on the cluster. In this study, radical-based reactions are occurring for both the positive and negative ion clusters with some evidence for silylene-based reactions. Surely one major reason for a differing mechanism is the strong interaction of WF_6 with either a positively or negatively charged center. This interaction is unlikely for methylsilane, which is neither strongly acidic nor strongly basic.

3.3.3. *Tungsten deposition*

Tungsten hexafluoride is used to deposit tungsten onto silicon as a barrier to diffusion of subsequentially deposited aluminium into the silicon substrate [27]. Recent studies have utilized only the silicon (i.e. no hydrogen as additional reductant) to reduce the tungsten hexafluoride to tungsten metal [4]. The question arises as to how the observed cluster ion reactions might apply to the reactions of tungsten hexafluoride with bulk silicon. Although a large variety of reaction products are observed for the smaller clusters, the larger clusters undergo simple monofluorination. If this latter reaction holds true for bulk

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* If insertion were involved in the multiple fluorinations, then the tungsten–silicon bond thus formed would be expected to remain intact.

** Formation of a silicon–fluorine bond could lower the energy separation between a closed and a ring-opened structure.

silicon, then tungsten deposition onto silicon, without use of an additional reductant, would involve the intermediacy of WF_5 following monofluorination of the surface. Thus, although the overall reaction

$$2\,WF_6 + 3\,Si(s) \rightarrow 3\,SiF_4 + 2W(s) \qquad \Delta H = -1400\ \text{kJ/mole} \qquad (10)$$

is highly exothermic, our study suggest that it proceeds through multiple steps. Even the intermediate WF_5 may simply monofluorinate the silicon surface since its W–F bond is weaker than WF_6 (cf. table 3).

4. Summary

Anionic and cationic silicon clusters (Si_{1-3}^{+} and Si_{1-5}^{-}) react exothermically with WF_6 to give a variety of tungsten and silicon fluorides. For the larger clusters (Si_{4-6}^{+} and Si_6^{-}), monofluorination of the silicon clusters is the sole product (excluding charge transfer for Si_6^{-}). The mechanism for reaction relies on formation of a complex between the silicon ion site and a fluorine on WF_6. Simple monofluorination of the clusters results from this interaction, whereas further fluorination appears to require an open cluster structure (created by the energy provided upon association) to make available a second radical site that abstracts fluorine. Formation of tungsten–silicon bonds probably occurs by silylene insertion into a tungsten–fluorine bond. Extrapolating to bulk silicon suggests that WF_6 primarily transfers a single fluorine atom. Further reaction with the surface to yield tungsten metal probably occurs through intermediates such as WF_5. The electron affinities of Si_{2-6} are less than the electron affinity of WF_6 (350 kJ/mole (3.6 eV)).

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