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The Chemical Exhaust Hazards of Dichlorosilane Deposits Determined with FT-ICR Mass Spectrometry

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Abstract — Flammable deposits have been analyzed from the exhaust systems of tools employing dichlorosilane (DCS) as a processing gas. Exact mass determinations with a high-resolution Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometer allowed the identification of various polysiloxane species present in such an exhaust flow. Ion-molecule reactions indicate the preferred reaction pathway of siloxane formation is through HCl loss, leading to the highly reactive polysiloxane that was detected in the flammable deposits.

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I. Introduction

Many chemical vapor deposition (CVD) process gasses are often quite reactive and must be handled with appropriate caution, particularly silane where the associated explosive hazards have been well studied and reviewed [1]. However, only little consideration has been given to direct combustion of dichlorosilane (DCS) [2,3]. Only one general discussion by McKinley mentions DCS and subatmospheric CVD "exhaust considerations" [4]. Semiconductor manufacturing involving DCS has revealed potential hazards in exhaust tubing and ductwork deposits, especially when they are disturbed by disassembly for cleaning [5]. Despite the use of nitrogen gas purging for dilution in the dry pumps and the exhaust stream, there is buildup of combustible and pyrophoric deposits in exhaust systems. McKinley's review points out that exhaust gas mixtures are not well understood and concludes that extensive combustion and/or scrubbing are required for a safe and clean exhaust plume [4].

In order to investigate the composition and chemical reaction pathways of this exhaust buildup, high-resolution Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry was utilized to analyze process exhaust samples. The exhaust samples were obtained both upstream and downstream of the vacuum pumps of a hot-wall silicon-oxide deposition process. To further elucidate reaction paths, controlled examination of some pertinent ion-molecule chemical reactions was performed, in particular the ion-molecule reactions between dichlorosilyl cations ($SiHCl_2^+$) and molecules of O_2, H_2O and N_2O were examined. Only in the water reactions were there products observed in a reasonable time and they are the focus of the discussion herein.

II. Experimental

FT-ICR mass spectrometric experiments were performed using a refurbished Finnigan FTMS-2000 that is described briefly [6]. The superconducting magnet has been rewired to a 3.3 Tesla field and much of the original equipment has been replaced by MIDAS electronics and data acquisition software [7]. A dual ion trap design was utilized, connection of them was provided by a centered 0.030" differential pumping hole. Pumping on both sides was provided by oil diffusion pumps (Sanovac-5 oil in Edwards Diffstak 160, 750 l/s for air), where base pressures were typically 3×10^{-9} Torr. An electron ionization beam traversed the dual trap to generate ions in either trap. Pairs of solenoid pulse valves allowed the controlled introduction of gas samples to either side of the ion trap. A typical experiment entailed pulsing of the DCS gas followed with the electron beam at ~ 20 eV; this generated $SiHCl_2^+$ and some SiH_2Cl^+. Resonance ion ejection was used to isolate the $SiHCl_2^+$ species. After a delay allowing the neutral DCS gas to be pump out, a second set of pulse valves introduced neutral gas to react with the trapped ions.

Process exhaust samples were obtained while the reactor was running at the process temperature both with and without a nitrogen purge gas. The container used to collect a sample was a special silicon oxide coated 1.8 liter stainless steel bulb (SilcoCan, Restek Corp.). The coating prevented degradation of the sample. The exhaust gas was introduced into the bulb and purged several times to passivate its surface before the final collection. Mass analysis of the samples occurred over the next week in two methods. The first method was direct introduction of the sample gas through pulsed valves, followed by ionization and detection on a short time scale (~ 0.2 s). The second method was pulsed introduction and ionization of a high pressure pulse of the exhaust gas, which was then allowed to undergo electron transfer (predominantly from N_2^+) and proton/hydride transfer while the pulsed sample pressure was being pumped. This second method allowed for the detection of some low concentration species that in general have low ionization potential, these typically being larger molecular species.

III. Results

The high-resolution capability of the FT-ICR instrument routinely allows milli amu (atomic mass unit) measurement. This usually allows exact molecular formula of the ions measured to be determined. Figure 1 is a section of two mass spectra, from m/z (mass/charge) = 97–104, showing the unreacted dichlorosilane in a CVD pump exhaust line, and compares the FT-ICR spectrum to that from a quadrupole mass spectrometer (UTI, model 100C). The dichlorosilane signal resulted from only a few percent DCS contained in the gas sample which was > 90% N_2. For resolution and speed the FT-ICR is superior; however, the dynamic range of the quadrupole mass spectrometer is better, resulting in a larger signal-to-noise. There are ways around this limitation of dynamic range; the simplest being to eject the largest ion species which leads to enhancement of the smaller ones.

The direct exhaust sample pulse/ionization/detection led only to the detection of the major exhaust gas components: N_2, N_2O, and SiH_2Cl_2. However, with sufficient pressure, upon collision of the dominant molecular nitrogen ion present (which has a high ionization potential, $IP_{N_2} = 15.58$ eV) with a lower IP species, charge transfer did readily occur. This resulted in ion signals for those species with the lowest ionization potential and lowest gas phase basicity, which were typically the more conjugated species that were at too low a concentration to be directly observed. The high-pressure pulse from the foreline exhaust sample, with delayed detection, allowed for these processes to occur to a great extent. This type of experiment resulted in the detection of many ions, summarized in Table I. The table identifies various chlorosilane, chlorosiloxane and siloxane ions by their exact masses. The mass scale was calibrated internally at four peaks: $SiCl^+$ (m/z = 63), $SiHCl^{37}Cl^+$ (m/z = 101), $Si_3O_2H_6Cl^+$ (m/z = 157) and $C_{19}H_{31}^+$ (m/z = 259).

Figure 2 shows the mass spectra resulting from the controlled reaction of dichlorosilyl cation with H_2O at two different stages of reaction, (a) midway and (b) nearly complete. Numbered mass peaks correspond to the ion products of the following reactions where the water reactions initially proceed to hydrolyze $SiHCl_2^+$, as follows:

$$SiHCl_2^+ + H_2O \longrightarrow SiHCl(OH)^+ + HCl \tag{1}$$

$$SiHCl(OH)^+ + H_2O \longrightarrow SiH(OH)_2^+ + HCl \tag{2}$$

$$SiH(OH)_2^+ + H_2O \longrightarrow Si(OH)_3^+ + H_2 \tag{3}$$

Reaction (3) was relatively slow and was only observed when the relative water pressure is much greater than the dichlorosilane pressure. Products from (1) and (2) were then observed to undergo further elimination reactions with DCS:

$$SiHCl(OH)^+ + SiH_2Cl_2 \longrightarrow H_2ClSiOSiHCl^+ + HCl \tag{4}$$

$$SiHCl(OH)^+ + SiH_2Cl_2 \longrightarrow HCl_2SiOSiHCl^+ + H_2 \tag{5}$$

$$SiH(OH)_2^+ + SiH_2Cl_2 \longrightarrow H_2ClSiOSiH(OH)^+ + HCl \tag{6}$$

$$SiH(OH)_2^+ + SiH_2Cl_2 \longrightarrow HCl_2SiOSiH(OH)^+ + H_2 \tag{7}$$

The channels resulting in the loss of HCl were at least 5 times faster than their competing H_2 loss channels, seen by the greater product intensities of reactions (4) and (6) vs. (5) and (7), respectively, in Figure 2. The resulting disiloxane species underwent complete hydrolysis when there was sufficient water and/or reaction time. Thus, the complete reaction equation is:

$$SiHCl_2^+ + SiH_2Cl_2 + 6\,H_2O \longrightarrow (OH)_3SiOSi(OH)_2^+ + 4\,HCl + 3\,H_2 \tag{8}$$

Further polymerization past disiloxane was not observed, possibly due to the low pressure of DCS in these experiments.

However, the presence of larger polysiloxanes was detected (as those from the exhaust gas samples) in the solid samples from several sections of the exhaust tubing analyzed by nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies. The flammable samples were typically orange/brown in color, becoming less reactive as the color lightened to tan, and finally unreactive when white. NMR study of the flammable samples indicated the presence of siloxane species $Si–(O–Si)_{3–4}$, this was supported by IR spectra indicating a strong Si–O–Si absorbance at 1110 cm^{-1}. The Si–O–Si signals in both NMR and IR spectra decreased as the sample color lightened and their reactivity decreased.

IV. Discussion and Conclusion

The use of high-resolution FT-ICR mass spectroscopy has led to the identification of many products in the exhaust flow of a DCS/N_2O oxide deposition process. The siloxane/chloro-siloxane exhaust gasses detected, as seen in Table I, are consistent with the solid flammable buildup determined to be mostly composed of various siloxane species. The ion reactions observed from Figure 2 indicate the formation of these siloxanes occurs when trace water is present along with DCS in the exhaust tubing. This reaction results mostly in chlorosiloxanol (similar to reaction 1) that will react with DCS to form dichlorodisiloxane (similar to reaction 4, again with preferential loss of HCl). The process of reaction with water and DCS can continue, creating larger polysiloxanes, until the polysiloxane molecule finally precipitates onto a surface. Further heterogeneous reactions likely occur on the surface, and even somewhat after being "covered".

This trapped polysiloxane precipitate now creates the main hazard of the DCS exhaust buildup because it is still reactive upon exposure to air/water. This hazard is exacerbated by the preferential loss of HCl in the DCS reactions with water seen by the ion reactions. The chorine depletion is also evidenced by the types of polysiloxanes detected in the exhaust gas, where at most there are three chlorine atoms detected in species containing three and four Si atoms. The resulting polysiloxanes are then more flammable due to their evolution of hydrogen gas upon reaction with air/water than those containing more chlorine atoms.

The kinetics of the various polysiloxane formation routes need to be further understood before an efficient preventative solution can be proposed to prevent the buildup of flammable residue. This data could be combined with the exhaust gas residence times to determine the minimum amount of scrubbing required. This should be of concern to any semiconductor manufacturer that utilizes DCS as a process gas and exhausts it into air ducting at significant concentrations (greater than about 0.1%).

Mass spectral examination of ion-molecule reactions of dichlorosilyl cation with H_2O in the ICR ion trap found the precursor species to those detected in a semiconductor process exhaust sample. These exhaust polysiloxanes were then found in the exhaust tubing as flammable solid precipitate, thereby confirming that the ion-determined reactions are occurring with DCS upon contact with ambient air. Further investigation of the reaction kinetics is in progress in order to determine, given exhaust gas residence times, an effective scrubbing process to eliminate this buildup of flammable residue.

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[1] V. M. Fthenakis and P. D. Moskowitz, "An assessment of silane hazards," *Solid State Technol.*, vol. 33, pp. 81–85, Jan. 1990.

[2] R. G. Aivazyan, V. V. Azatyan, V. I. Kalachev, and T. A. Sinel'nikova, "Stable products and some kinetic features of dichlorosilane-air combustion," *Kinetics and Catalysis*, vol. 36, pp. 168–173, 1995.

[3] K. G. Sharp, A. Arvidson, and T. C. Elvey, "Hazard potential of dichlorosilane," *J. Electrochem. Soc.*, vol. 129, pp. 2346–2349, Oct. 1982.

[4] R. J. B. McKinley, "Vacuum equipment exhaust considerations for subatmospheric pressure CVD applications," *Solid State Technol.*, vol. 30, pp. 119–122, Aug. 1987.

[5] Private communications with Intel Corporation.

[6] For a review of fundamental FT-ICR theory and application see: A. G. Marshall, C. L. Hendrickson, and G. S. Jackson, "Fourier-transform ion-cyclotron resonance mass-spectrometry: A primer," *Mass Spectrom. Rev.*, vol. 17, pp. 1–35, Jan.–Feb. 1998.

[7] MIDAS (Modular ICR Data Acquisition and Analysis System) is a product of the FT-ICR/MS group at the National High Magnetic Field Laboratory, Florida State University.

TABLE I

Silicon Species Identified from Exhaust Stream

Ion formula	Ion exact mass (amu)	Measured mass (amu)	Mass error (amu x 1000)
$HSi{=}O$	44.97967	44.97947	-0.20
$SiCl$	62.94578[a]	62.94581	0.03
$Si^{37}Cl$	64.94283	64.94269	-0.14
$SiHCl_2$	98.92246	98.92189	-0.57
$SiHCl^{37}Cl$	100.91951[a]	100.91924	-0.27
Si_2H_2OCl	108.93327	108.93352	0.25
Si_2H_4OCl	110.94892	110.94878	-0.14
$Si_2H_5Cl_2$	130.93069	130.93151	0.82
$Si_2H_5Cl^{37}Cl$	132.92774	132.92690	-0.84
$Si_3H_5O_3$	136.95465	136.95442	-0.23
$Si_2H_3OCl_2$	144.90995	144.91066	0.71
$Si_2H_3OCl^{37}Cl$	146.90700	146.90628	-0.72
$Si_3H_6O_2Cl$	156.93642[a]	156.93720	0.78
$Si_3H_6O_2{}^{37}Cl$	158.93347	158.93329	-0.18
$Si_2H_4Cl_3$	164.89172	164.89048	-1.24
$Si_2H_4Cl_2{}^{37}Cl$	166.88876	166.88721	-1.55
Si_4H_7O	182.94212	182.94118	-0.94
$Si_3H_5O_2Cl_2$	190.89744	190.89759	0.15
$Si_3H_5O_2Cl^{37}Cl$	192.89450	192.89531	0.81
$Si_4H_8O_3Cl$	202.92391	202.92358	-0.33
$Si_4H_8O_3{}^{37}Cl$	204.92096	204.92265	1.69
$Si_3H_6OCl_3$	210.87921	210.87925	0.04
$Si_3H_6OCl_2{}^{37}Cl$	212.87626	212.87629	0.03
$Si_4H_6O_4Cl$	216.90318	216.90444	1.26
$Si_4H_6O_4{}^{37}Cl$	218.90023	218.90097	0.74
$Si_5H_9O_5$	228.92964	228.92812	-1.52
$Si_4H_7O_3Cl_2$	236.88494	236.88474	-0.20
$Si_4H_7O_3Cl^{37}Cl$	238.88199	238.87836	-3.63
$Si_5H_7O_6$	242.90891	242.90800	-0.91
$Si_5H_{10}O_4Cl$	248.91140	248.91148	0.08
$Si_4H_6O_3Cl_3$	270.84597	270.84603	0.06
$Si_4H_6O_3Cl_2{}^{37}Cl$	272.84301	272.83897	-4.04
$Si_6H_{11}O_6$	274.91713	274.92084	3.71
$Si_5H_7O_5Cl_2$	296.85170	296.85051	-1.19
$Si_5H_7O_5Cl^{37}Cl$	298.84874	298.84675	-1.99

[a] These ion masses (as well as $C_{19}H_{31}$ measured at 259.24178) used as internal mass calibration points for whole spectrum.

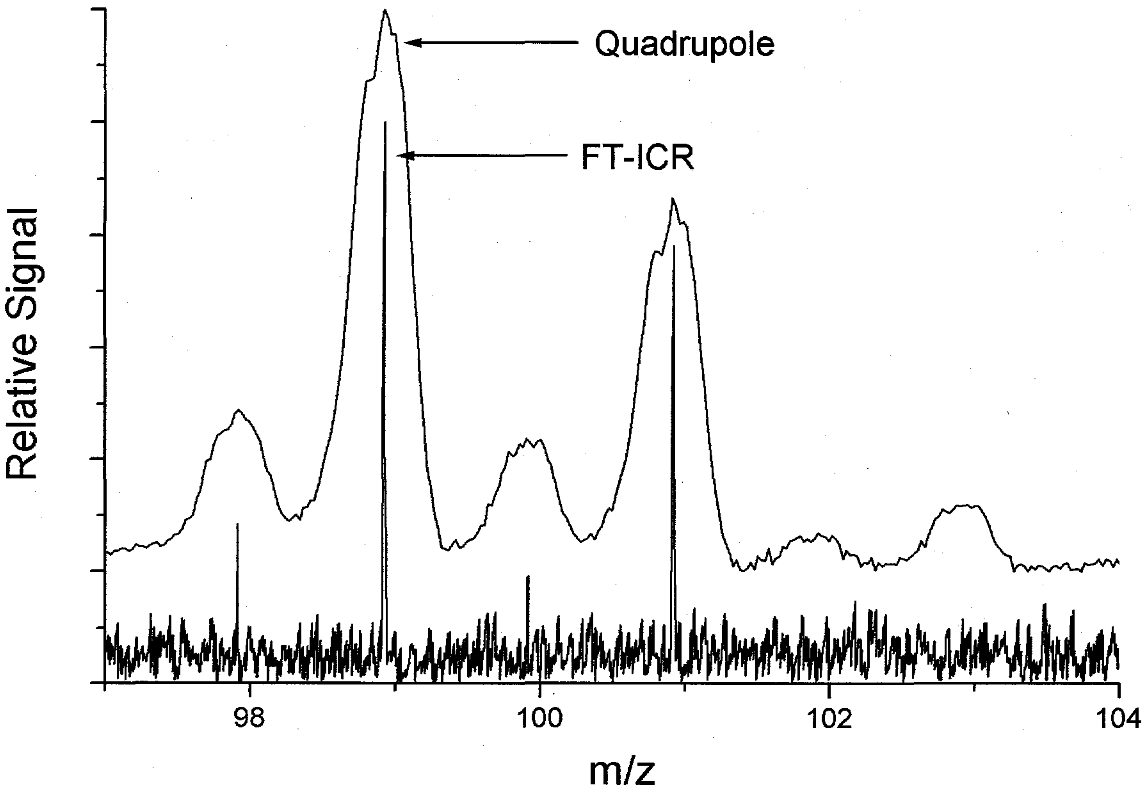

Fig. 1: Jarek and Thornberg

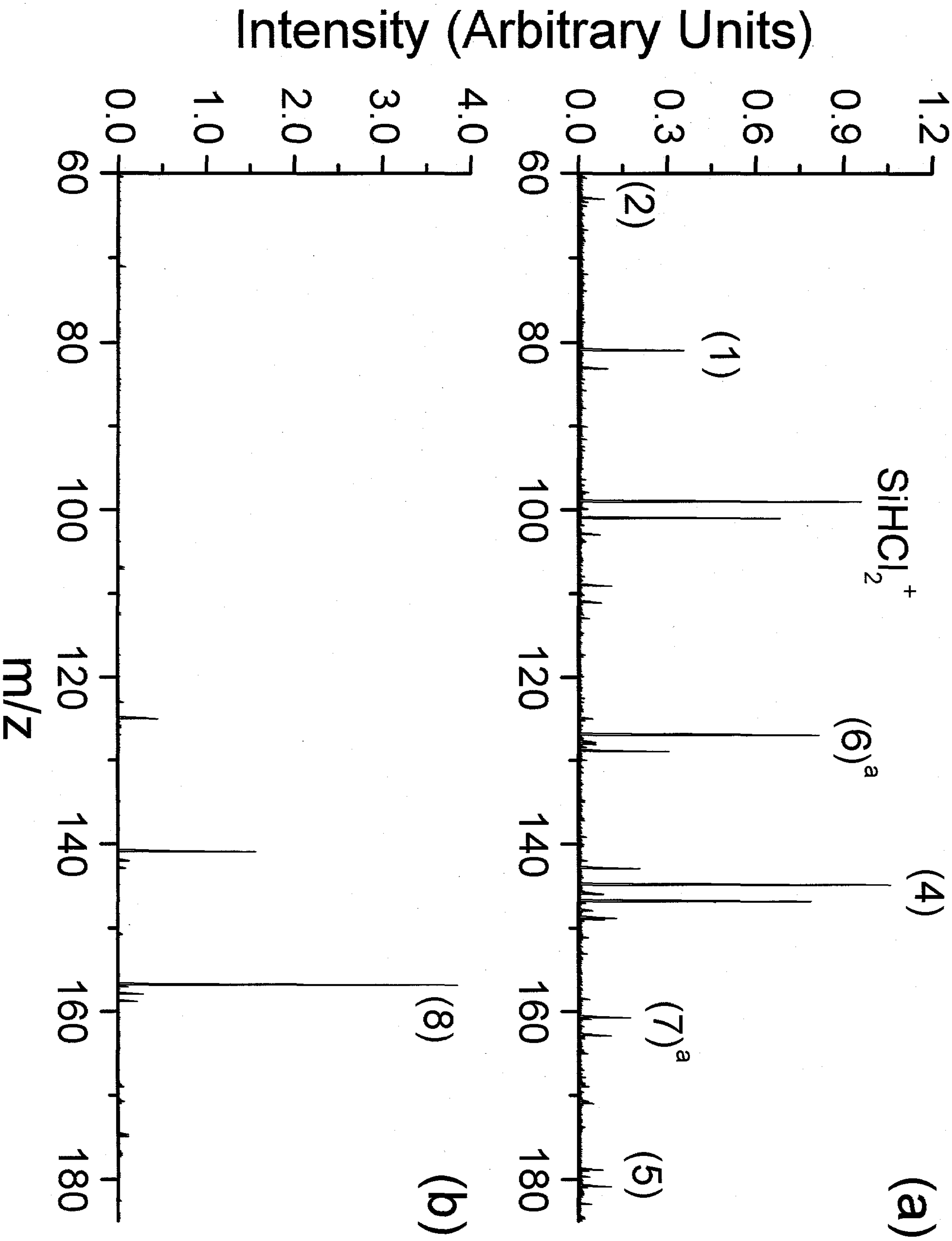

Fig. 2: Jarek and Thornberg

Figure 1. Comparison of the resolution capability and dynamic range of the FT-ICR vs. quadrupole mass spectrometry.

Figure 2. Reaction FT-ICR spectra of $SiHCl_2^+$ with H_2O at two time sections: (a) middle of reaction course, (b) near end of reaction. Numeric labels correspond to the product ions from reactions given in the text. Noted products, $( )^a$, have other routes of formation.