creased ceramic yields. Another fact less emphasized is that pyrolysis gases from these organic groups are evolved primarily at higher temperatures. This becomes a critical issue when fabricating parts from these preceramic polysilazanes. As the temperature increases, the pyrolytic residues become increasingly more rigid and the nondestructive, controlled removal of the gaseous products becomes more difficult.

Acknowledgment. We thank Bruce Smith and Garry Garvey of AKZO Chemicals, Dobbs Ferry, NY, for their assistance with some of the mass spectrometry measurements. The generous support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. SiC, 409-21-2; Si_3N_4, 12033-89-5; Cl_3SiH, 10025-78-2.

Thermogravimetric Mass Spectrometric Investigation of the Thermal Conversion of Organosilicon Precursors into Ceramics under Argon and Ammonia. 1. Poly(carbosilane)

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The pyrolysis under argon and under ammonia of Yajima's poly(carbosilane) (PCS) was studied by means of thermogravimetric analysis associated with continuous mass spectrometry of the gases evolved. The degradation of the polymer skeleton under argon leads to the evolution of methylsilanes and higher linear oligomers; the escape of hydrogen starts simultaneously. Mechanisms of pyrolysis are proposed, which involve in a first step the homolytic cleavage of Si–H and Si–C bonds in the poly(carbosilane) skeleton. Under ammonia, amination and carbon removal (mainly as methane) start well below the thermal decomposition of ammonia. The first step likely corresponds to the nucleophilic substitution of Si–H bonds by ammonia; Si–C bonds are substituted at higher temperature, and homolytic cleavages are probably involved. However, H-abstraction from N–H bonds hinders the cross-linking via Si–Si and Si–C-Si bridges, thus allowing complete nitridation.

Introduction

Since the early work of Verbeek[1] and Yajima,[2] the preparation of silicon carbide and silicon nitride ceramics by pyrolysis of organosilicon polymers has led to numerous publications, which have been reviewed by several authors.[3-5] Insights into the thermolysis chemistry are necessary in order to choose suitable polymeric precursors as well as to set up the procedure of the pyrolysis step, such as the temperature, the heating rate, and the atmosphere (inert or reactive gas, or vacuum). In practice, the use of a reactive atmosphere may drastically modify the nature of the ceramic material for a given precursor.

Thus, the production of SiC Nicalon fiber first developed by Yajima et al.[1,6] was based on the curing of poly(carbosilane) (PCS) fiber by heating in air. This oxidation stage makes the melt-spun PCS fiber infusible before its final conversion into ceramic at higher temperatures under nitrogen. The oxygen introduced during the curing step is still present after the pyrolysis, and the continuous phase in the final fiber is actually an amorphous silicon oxycarbide phase.[7]

Pyrolysis under an ammonia atmosphere has been also used.[8,9] It completely changes the elemental composition of the ceramic material by removing carbon and incorporating nitrogen. Thus, PCS cured either by electron irradiation[8] or thermally[9] is converted to silicon nitride by pyrolysis in ammonia, whereas PCS cured by oxidation leads to silicon oxynitride.[8] The pyrolysis in ammonia may also be used to remove the excess carbon from SiC or Si_3N_4 ceramic powders.[10] Many papers have been devoted to the thermal conversion of PCS under argon. The structural evolution of the materials during the pyrolysis was investigated by IR, NMR, and X-ray absorption spectroscopy,[11-14] while the analysis of the volatile products was

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Table I. Ceramic Yields, Elemental Analysis, and Silicon Loss for PCS Pyrolyzed at 1350 °C in Argon, and at 750 and 1350 °C in an Ammonia–Argon Mixture (30/70 v/v)

conditions	yield, %	% Si	% C	% H	% O	% N	$\Delta Si/Si_p$, %
1350 °C, Ar	42	57.4	38.2	0.2	1.3		52
750 °C, Ar/NH_3	61	48.2	7.2	3.7	2.6	36.6	41
1350 °C, Ar/NH_3	54	56.2	4.8	0.4	4.8	37.3	39

carried out by GC and MS[15,16] and by gas evolution measurements[17] in addition to the usual thermal analysis methods (TGA, DTA). The thermal conversion of PCS under ammonia was investigated mainly by NMR spectroscopy,[18] by elemental analysis,[8,9] and thermogravimetry.[8]

Some mechanisms have been proposed for the cross-linking and the mineralization of PCS,[17,13] but very little has been done concerning its thermal fragmentation in argon or in ammonia, although this step governs the ceramic yield.[3] As to the nitridation of PCS, it is not known whether it proceeds via nucleophilic attack of ammonia[5] or by reactions involving the NH_2 radicals, generated during the decomposition of ammonia.[9] In this work we investigated the thermal reactivity of PCS in argon and in ammonia, by means of thermogravimetric analysis associated with the continuous mass spectrometry of the gases evolved during pyrolysis (TG/MS analysis). TG/MS analysis is a valuable tool for investigating the thermal reactions occuring during the pyrolysis of ceramic precursors; it complements the information gained by other essential techniques, such as elemental analysis and solid-state NMR.

Experimental Section

Materials. The PCS used for this study originated from Dow Corning (PC X9-6348); according to gel permeation chromatography (GPC) its number average molecular weight (M_n) relative to polystyrene standards is 1420 g mol^{-1} and its weight average molecular weight (M_w) is 3030 g mol^{-1} (see Figure 2). Elemental analysis led to the following atomic compositions: $SiC_{1.95}H_{4.7}$. According to Soraru et al.,[12] this polymer is mainly built of $-Si(CH_3)_2CH_2-$ and $-Si(CH_3,H)CH_2-$ units in a 1/1 ratio, although a significant amount of cross-linking units is certainly present.[19]

We chose to study PCS without further cross-linking in order to avoid the presence of oxygen atoms.

Techniques. *TG/MS Analysis.* Thermogravimetric analysis (TGA) was carried out using a Netzsch STA409 thermobalance. Typically about 20 mg of sample was heated in an alumina crucible from room temperature to 1200 °C at 10 K min^{-1} in a stream of pure argon or an ammonia–argon (30/70) mixture (flow rate 50 mL min^{-1}) to avoid the presence of ammonia in the balance section.

The thermogravimetric analyzer was coupled to an Anagaz 200 Delsi Nermag quadrupole mass spectrometer (ionization energy 75 eV). The volatile products evolved during pyrolysis were sampled above the crucible by a stainless steel capillary (internal diameter 0.25 mm) heated at 150 °C. The capillary is connected to the mass spectrometer through a 32-μm molecular leak. A scan from 2 to 150 amu was collected and stored every 30 s throughout the pyrolysis process. This apparatus permits the identification of the different gases evolved during pyrolysis; it is possible either to plot mass spectra obtained at selected temperatures or to plot the evolution of the signal of characteristic ions as a function of temperature. In the absence of standardization only qualitative information may be drawn from these curves. It should be noted that, due to the limited range of the mass spectrometer and to condensation in the cold parts of the apparatus, only low molecular weight compounds such as gases or volatile liquids are detected by TG/MS. Thus, a release of condensable compounds such as oligomers may not be detected by MS despite a noticeable weight loss in the TGA curve.

Table II. Weight Composition of the Ceramics after Pyrolysis at 1350 °C in Argon and in an Ammonia–Argon Mixture (30/70 v/v), According to the Rule of Mixture Calculations[7]

atmosphere	% SiO_2	% Si_3N_4	% SiC	% C
Ar	2.5		83.0	14.5
Ar/NH_3 (70/30)	8.4	87.1		4.5

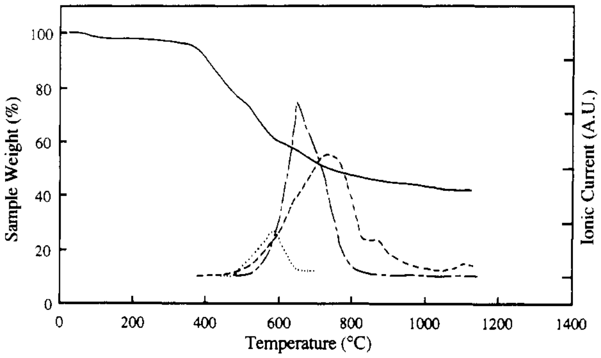

Figure 1. TG/MS analysis under argon of PCS. (—) TGA curve; the ion signal at m/z 2 (– – –) arises from hydrogen; m/z 16 (- — -) arises from methane; m/z 59 (···) corresponds to $SiMe_2H^+$ and arises from Me_2SiH and Me_3SiH.

Elemental Analyses. Elemental analyses were performed by the Service Central d'Analyses du CNRS in France. The samples were heated in an ammonia–argon atmosphere (30/70) using a temperature program of 10 °C/min to the specified temperature.

Gel Permeation Chromatography. Gel permeation chromatography (GPC) was performed in tetrahydrofuran (flow rate 1 cm^3/min) using a Waters apparatus (Ultrastyragel columns, 100, 500, 1000, and 10 000 Å, pump EF410, refractive index detector) and polystyrene standards.

Results

Elemental Analysis and Ceramic Yield. Table I shows the ceramic yields and compositions of pyrolysed PCS after heating to 1350 °C under argon.

Loss of Silicon. The ceramic yields are quite low, indicating a significant loss of organosilicon species. The loss of silicon during the pyrolysis, ΔSi, may be calculated according to

$$\Delta Si = Si_P - YSi_c$$

where Si_P is the wt % silicon content of the starting precursor, Si_c the wt % silicon content of the final ceramic, and Y the ceramic yield. The relative loss of silicon, $\Delta Si/Si_p$ calculated for each case (argon and ammonia) is reported in Table I. These values show that the loss of silicon is significantly lower when the samples are pyrolyzed in ammonia, (40% compared to 52%).

Excess of Carbon. The composition of the residues at 1350 °C, assuming that only equilibrium phases, SiO_2, SiC, Si_3N_4, and C, are present in the final ceramic (rule of mixture calculations[7]), is reported in Table II. These calculations allow the evaluation of the amount of excess carbon in the ceramic. As expected the composition of the sample pyrolysed under argon corresponds to SiC with an excess of carbon of ca. 15%; under ammonia the composition is close to Si_3N_4 with a final carbon content much lower than under argon. Elemental analyses also show

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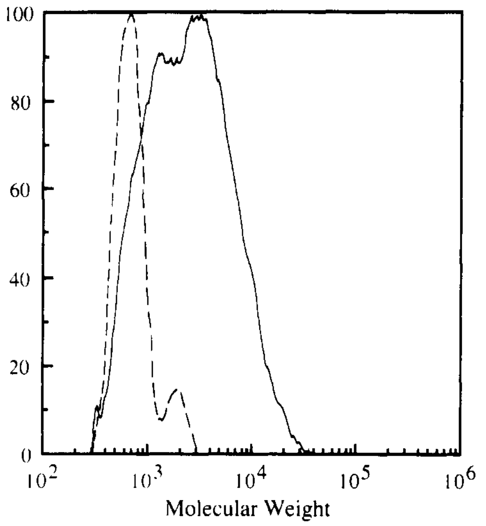

Figure 2. GPC analysis of PCS (—) and of the volatile fraction collected by vacuum distillation at 300 °C (---) (molecular weights relative to polystyrene standards).

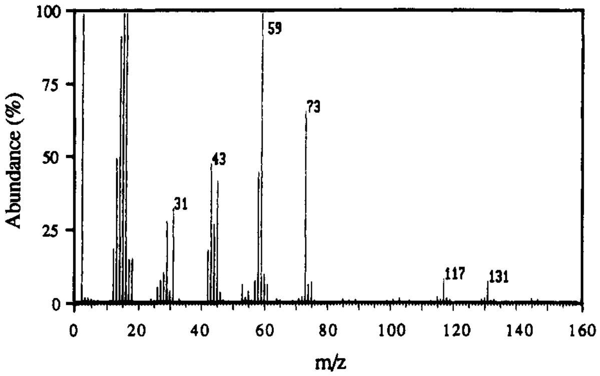

Figure 3. Mass spectrum of the gases evolved at 570 °C during the pyrolysis of PCS under argon.

that, at 750 °C, most of the carbon is removed and that the amination is complete (actually there is even an excess of nitrogen at 750 °C compared to 1350 °C).

TG-MS Analysis. Under argon (Figure 1), TGA curve shows a large weight loss (ca. 23%) from 350 to 475 °C; no gaseous species are detected by mass spectrometry until 475 °C, indicating that this first loss possibly corresponds to the distillation of volatile oligomers, which further condense in the cold parts of the apparatus. Indeed, the PCS sample used has a very low number average molecular weight: M_n = 1420 g mol^{-1}. The GPC curves displayed in Figure 2 shows that about 24% of the sample has a molecular weight lower than 1000 g mol^{-1}. By vacuum distillation (300 °C, 0.1 Torr) a volatile fraction representing about 19 wt % of the PCS was collected; the GPC analysis of this fraction, reported in figure 2, gave the following average molecular weights (relative to polystyrene standards): M_n = 655 g mol^{-1}; M_w = 905 g mol^{-1}. This result confirms that most of the weight loss occuring below 475 °C may be ascribed to the distillation of the low molecular weight oligomers initially present in PCS.

In the temperature range 475–650 °C, a 21% weight loss is recorded, and a large release of organosilicon compounds is detected, as shown by the spectrum recorded at 560 °C which is displayed in Figure 3. Comparison with mass spectral data for silane and the methylsilanes[20] (Table III) indicates that this spectra very likely corresponds to a mixture of Me_3SiH, Me_2SiH_2, and possibly $SiMe_4$ and $MeSiH_3$. The formation of SiH_4, which was previously assumed,[15] is not detected; indeed in all the spectra *m/z* 30 is much less abundant than *m/z* 31, contrary to what would be expected for SiH_4 (Table III). Fragments at *m/z* 117 and 131 correspond to $Me_2HSiCH_2SiMeH^+$ and $Me_2HSiCH_2SiMe_2{}^+$ ions, which are the base ions in the spectra of $Me_2HSiCH_2SiMe_2H$ and $Me_3SiCH_2SiMe_2H$, respectively.[21a] Cyclic dimers, such as 1,3-dimethyl-1,3-disilacyclobutane (base ion at *m/z* 101) or 1,1,3-trimethyl-1,3-disilacyclobutanes (base ion at *m/z* 115) are not observed.[21b] Higher oligomers are possibly formed during the pyrolysis of PCS, but the limited range of our mass spectrometer as well as condensation in the cold parts of the furnace preclude their detection. It is noteworthy that hydrogen is detected only above about 475 °C.

The third weight loss (ca. 14% from 650 to 1150 °C) originates mainly from a loss of methane (*m/z* 14–16) between 500 and 820 °C and hydrogen; a small escape of C_2 hydrocarbons is also detected from 500 to 700 °C. It must be added that, due to the melting of PCS before its thermal cross-linking, escape of pyrolysis gases is somewhat discontinuous, leading to poorly reproducible shapes for the peaks of methane and the methylsilanes.

Table III. Monoisotopic Mass Spectra of Silane, Methylsilanes, and Trimethylsilylamine (from Refs 20 and 22)

m/z	SiH_4	$MeSiH_3$	Me_2SiH_2	Me_3SiH	Me_4Si	Me_3SiNH_2
28	23.0	24.9	24.3	5.0	1.7	
29	23.4	9.3	13.6	8.4	5.2	
30	100.0	21.5				
31	78.2	11.3	24.5	14.1	3.0	
40	0.3	2.1				
42		17.6	16.9	6.5	2.4	
43		43.4	54.9	23.4	10.7	10.0
44		100.0	57.6		7.0	26.0
45		66.8	70.2	13.5	16.0	
46		0.6				12.2
53					1.7	
57			7.0	5.2		
58			75.0	21.6		
59			100.0	100.0	2.8	
60						3.0
73				54.6	100.0	2.7
74						100.0
89						4.7

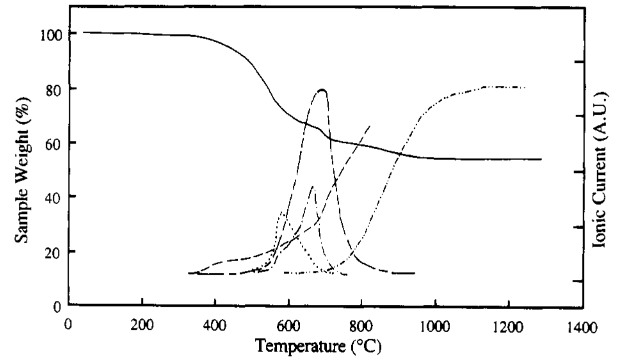

Figure 4. TG/MS of PCS analysis under ammonia/argon (30/70). (—) TGA curve; the ion signal at *m/z* 2 (---) arises from hydrogen; *m/z* 13 (-—-) arises from methane; *m/z* 59 (···) corresponds to $SiMe_2H^+$ and arises from Me_2SiH and Me_3SiH; *m/z* 74 (-··-) corresponds to $SiMe_2NH_2{}^+$ and arises from Me_2HSiNH_2 or Me_3SiNH_2; *m/z* 28 (-···-) corresponds to N_2 arising from the dissociation of ammonia.

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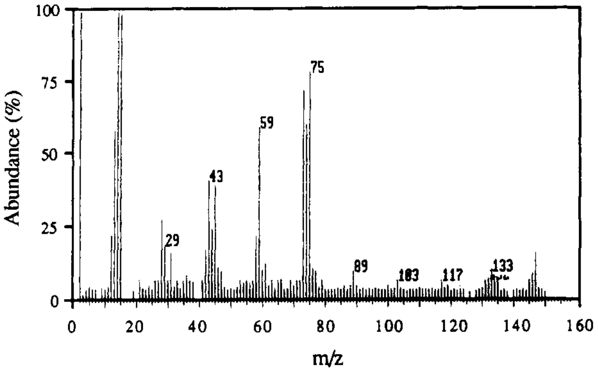

Figure 5. Mass spectrum of the gases evolved at 610 °C during the pyrolysis of PCS under ammonia/argon (30/70).

Additional experiments were carried out on a PCS sample cross-linked by thermal treatment (5 h at 250 °C) under argon. The ceramic yield was increased, but the gases detected were the same.

TG-MS Analysis under Ammonia. As mentioned above, the pyrolysis was conducted under a flow of argon and ammonia (30/70), at a heating rate of 10 °C/min. These conditions are of course not the most suitable to obtain pure silicon nitride (which was not the aim of this work), but they are the most suitable to obtain a dynamic picture of the thermal processes occurring during the pyrolysis.

The thermal behavior of PCS is modified in the presence of ammonia, as shown in Figure 4. A small escape of hydrogen is detected above 360 °C (instead of 450 °C under argon). On the other hand, the temperature range for the escape of methane is not modified (the detection of methane is based on mass 13 in order to distinguish it from ammonia[23]). The thermal decomposition of ammonia into nitrogen and hydrogen is negligible below 650 °C, as indicated by the nitrogen evolution. Above 700 °C, a negligible escape of HCN (*m/z* 26, 27) was detected. Further features of pyrolysis under ammonia emerge from examination of the mass spectrum of the volatile silanes evolved around 600 °C (Figure 5). Release of methylsilanes from PCS between 500 and 730 °C is again observed, with abundant ions at *m/z* 59 and 73. In addition abundant ions at *m/z* 74 and 75 (and, to a lesser extent, *m/z* 89) shows the formation of aminomethylsilanes such as Me_3SiNH_2[22] and $Me_2Si(NH_2)_2$. Fragments at higher *m/z* ratios (134, 147, etc.) are also detected which very likely arise from nitrided fragments of PCS.

Discussion

Pyrolysis under Argon. The escaping gases detected by TG/MS analysis (H_2, CH_4, Me_3SiH, etc.) arise from condensation reactions between the various functional groups (Si-H, Si-CH_3, C-H, Si-CH_2-Si···) present in the precursors. The high temperatures required for the thermolysis of PCS (about 500–800 °C) are comparable to those used for the pyrolysis of Et_3SiH (480 °C),[24] Me_3SiH (660–710 °C),[25,26] or $SiMe_4$ (700 °C).[27] The gas-phase pyrolysis of trimethylsilane, Me_3SiH, was investigated by means of mass spectrometry;[25,26] these studies provide a good background for the understanding of the pyrolysis of PCS, with some modifications related to the presence of Si–CH_2–Si linkages, and the radical mechanisms proposed reasonably apply here. Indeed, the PCS sample used for this study contains no significant amount of Si–Si bonds,[12] and no SiH_2 or SiH_3 groups are present; thus the formation of silylene intermediates is unfavorable.[29]

It was previously assumed that the bond energy of Si–H was the lowest among the chemical bonds in polycarbosilane,[13] which is not consistent with the nearly equal bond energies for Si–C and Si–H reported in the literature.[25,28] Our experiments show that the escape of hydrogen and the loss of methylsilanes start at the same temperature, at about 475 °C, whereas the escape of methane is observed above 500 °C. This indicates that the cleavage of the Si–C bonds in the polycarbosilane skeleton, like that of the Si–H bonds (reactions 1a, 1b) occurs at a slightly lower temperature than the cleavage of Si–Me bonds (reaction 1c).

$$\equiv\text{Si—H} \rightarrow \equiv\text{Si}^{\bullet} + \text{H}^{\bullet} \tag{1a}$$

$$\equiv\text{Si—CH}_2\text{—Si}\equiv \rightarrow \equiv\text{Si}^{\bullet} + {}^{\bullet}\text{CH}_2\text{—Si}\equiv \tag{1b}$$

$$\equiv\text{Si—CH}_3 \rightarrow \equiv\text{Si}^{\bullet} + {}^{\bullet}\text{CH}_3 \tag{1c}$$

The radicals formed may then abstract hydrogen atoms to give H_2, CH_4, SiH, and $SiCH_3$ groups. Tetrasubstituted atoms such as silicon or carbon atoms are almost never abstracted by free radicals,[30] mainly due to steric hindrance; thus the abstraction of an entire group such as CH_3 or SiR_3, which is often postulated, is quite unlikely. Hydrogen may be abstracted either from Si–H bonds as in reaction 2a or from C–H bonds (reaction 2b) (where R = H, CH_3, ≡Si, CH_2-Si≡).

$$\text{R}^{\bullet} + \text{H—Si}\equiv \rightarrow \text{RH} + \equiv\text{Si}^{\bullet} \tag{2a}$$

$$\begin{aligned}&\text{R}^{\bullet} + \text{CH}_3\text{—Si}\equiv\ (\equiv\text{Si—CH}_2\text{—Si}\equiv) \rightarrow\\ &\qquad \text{RH} + {}^{\bullet}\text{CH}_2\text{—Si}\equiv\ (\equiv\text{Si—}{}^{\bullet}\text{CH—Si}\equiv)\end{aligned} \tag{2b}$$

The abstraction of hydrogen attached to carbon as in reaction 2b should take place at higher temperature[25] because the C–H bond is stronger than the Si–H bond: Reaction 1b leads to the cleavage of the poly(carbosilane) skeleton and, after H abstraction (reactions 2), to the formation of Si–H and Si–CH_3 chain ends (Scheme I). The escape of the various methylsilanes and of the linear oligosilmethylenes detected may easily be accounted for by successive cleavages of the carbosilane linkages followed by H abstractions (Scheme I). In the case of polysiloxanes, the main degradation mechanism consist in concerted redistribution of Si–O bonds, with formation of volatile, cyclic oligomers.[31] In the case of PCS, the escape of cyclic oligomers (1,3-disilacyclobutanes, 1,3,5-trisilacyclohexanes, etc.) is not observed, which suggests that the degradation of PCS through concerted redistribution reactions of Si–C bonds in the skeleton does not occur; the Si–C bonds actually rearrange much less easily than Si–O bonds.[32]

The combination of the various ≡Si$^{\bullet}$ and ≡C$^{\bullet}$ radicals formed in reactions 1 and 2 leads to the formation of Si–Si, Si–C, and C–C bonds, according to

$$\text{R}^{1\bullet} + \text{R}^{2\bullet} \rightarrow \text{R}^1\text{R}^2 \quad (\text{where R}^{\bullet} = \equiv\text{Si}^{\bullet}, \equiv\text{C}^{\bullet}) \tag{3}$$

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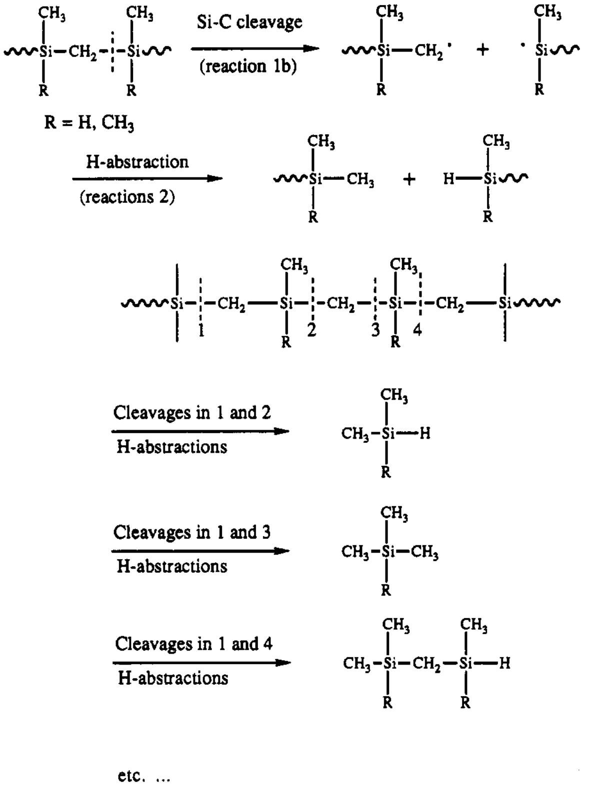
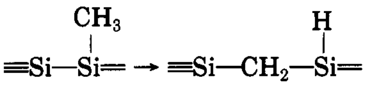
Scheme I. Schematic Representation of the Thermal Fragmentation of PCS under Argon



At high temperatures, the probability of Si–C and Si–H bond cleavage is high, the concentration of radicals becomes significant, and such combination reactions cannot be neglected. Note that the Si–Si bonds are unstable at the temperatures required by these reactions (T > 475 °C)[17] and that they very likely rearrange to more stable Si–C–Si bonds, for example through a methylene insertion as in the well-known Kumada's rearrangement:[33]



$$\equiv\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{Si}}}-\mathrm{Si}= \rightarrow \equiv\mathrm{Si}-\mathrm{CH_2}-\overset{\mathrm{H}}{\overset{|}{\mathrm{Si}}}= \qquad (4)$$

Reactions 3 lead to cross-linking of the polymer, which hinder the escape of organosilicon species.[3] However, the hydrogen and methane evolution shows that this cross-linking occurs above 475 °C only: thus after the distillation of low molecular weight chains, which starts at about 300 °C, and in the same temperature range as the degradation of the chain backbone, as shown by the escape of organosilicon fragments. This explains the high loss of silicon observed (52%). Indeed, this loss of silicon would be much higher unless there is significant initial cross-linking of PCS.[16,34]

Mineralization takes place above 500 °C, with a large escape of methane which indicates the occurrence of reactions 1c followed by H abstraction. The C–H bonds are the strongest bonds present in PCS, and their cleavage according to (5) require high temperatures:

$$\equiv\mathrm{C}-\mathrm{H} \rightarrow \equiv\mathrm{C}^{\bullet} + \mathrm{H}^{\bullet} \qquad (5)$$

Reaction 5 probably accounts for most of the hydrogen escape above 800 °C, and for the formation of unsaturated carbon atoms.[16]

Pyrolysis under Ammonia. Recent work has dealt with the pyrolysis of polymeric precursors under ammonia. It was shown that in the case of PCS carbon removal and amination occur simultaneously in the range 400–700 °C.[9] However the question arose whether the cleavage of Si–C bonds involves nucleophilic attack of NH_3 molecules[5] or radical reactions of the intermediates generated during the thermal decomposition of ammonia (reaction 6).[9,35]

$$2\mathrm{NH_3} \rightarrow \mathrm{N_2} + 3\mathrm{H_2} \qquad (6)$$

Elemental analysis and NMR spectroscopy showed that amination of PCS was nearly complete at 600 °C.[9,18] According to our experiments, the dissociation of ammonia is negligible below 650 °C, whereas aminated fragments are detected as low as 500 °C; thus, the main amination processes do not involve intermediates generated during the decomposition of NH_3.

The escape of hydrogen starts at 360 °C, about 90 °C lower than under argon. This behavior suggests that the first step of the amination process corresponds to the nucleophilic substitution of hydrogen atoms bonded to silicon by ammonia (eq 7); this mechanism is quite favorable in the case of the Si–H bond, which is sensitive to nucleophilic substitution.[36]

$$\equiv\mathrm{Si}-\mathrm{H} + \mathrm{NH_3} \rightarrow \equiv\mathrm{Si}-\mathrm{NH_2} + \mathrm{H_2} \qquad (7)$$

This result is consistent with previous observations that the Si–H bonds of PCS are more reactive towards ammonia than Si–C bonds.[9,18] The substitution of an H atom by an amino group should lead to a gain in weight; however, this reaction occurs at the same time as the distillation of low molecular weight oligomers, and an overall weight loss results, but smaller than under argon.

The main hydrocarbon detected is methane, which could arise from the substitution of methyl groups by NH_3 according to[5]

$$\equiv\mathrm{Si}-\mathrm{CH_3} + \mathrm{NH_3} \rightarrow \mathrm{Si}-\mathrm{NH_2} + \mathrm{CH_4} \qquad (8)$$

The complete amination of silicon would also imply the substitution of methylene groups in the poly(carbosilane) skeleton:

$$\equiv\mathrm{Si}-\mathrm{CH_2}-\mathrm{Si}\equiv + \mathrm{NH_3} \rightarrow \mathrm{Si}-\mathrm{NH_2} + \equiv\mathrm{Si}-\mathrm{CH_3} \qquad (9)$$

However, our results show that the escape of methane and organosilicon species start at the same temperature as under argon, which indicates that homolytic cleavages certainly take place; in addition, the reactivity of the Si–C bond toward nucleophilic substitution is much lower than that of the Si–H bond. Accordingly, above 500 °C a radical amination mechanism should be considered:

$$\equiv\mathrm{Si}-\mathrm{R} \rightarrow \equiv\mathrm{Si}^{\bullet} + \mathrm{R}^{\bullet} \quad (\mathrm{R} = \mathrm{H}, \mathrm{CH_3}, \mathrm{CH_2}-\mathrm{Si}\equiv) \qquad (1)$$

$$\mathrm{R}^{\bullet} + \mathrm{NH_3} \rightarrow \mathrm{RH} + {}^{\bullet}\mathrm{NH_2} \qquad (10a)$$

$$\equiv\mathrm{Si}^{\bullet} + {}^{\bullet}\mathrm{NH_2} \rightarrow \equiv\mathrm{Si}-\mathrm{NH_2} \qquad (11a)$$

It was shown that the thermal cross-linking of PCS under argon above 600 °C limited the further amination[9] by pyrolysis in ammonia, which is consistent with the fact that silicon carbide is not attacked by ammonia.[10] If homolytic cleavages of Si–C and Si–H bonds occur, cross-linking reactions similar as those proposed for the pyrolysis

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under argon should take place and should prevent a complete amination. However, easy, complete amination is observed. This may be explained by the possibility of abstraction of hydrogen atoms from N–H bonds, either on NH_3 molecules (reaction 10a) or on $SiNH_2$ and SiNHSi groups:

$$R^{\bullet} + {\equiv}SiNH_2 \rightarrow RH + {\equiv}SiNH^{\bullet} \qquad (10b)$$

$$R^{\bullet} + {\equiv}SiNHSi{\equiv} \rightarrow RH + ({\equiv}Si)_2N^{\bullet} \qquad (10c)$$

$$(R^{\bullet} = {\equiv}Si^{\bullet}, {}^{\bullet}CH_3, {}^{\bullet}CH_2Si{\equiv}, H^{\bullet})$$

In view of the abundance of H atoms arising from N–H bonds, reactions 10 must compete efficiently with other H-abstraction reactions (reactions 2); thus, ammonia favors the escape of methane and silanes.[37] In addition, amination of the silicon by combinations of $\equiv Si^{\bullet}$ radicals with $=N^{\bullet}$ radicals (reactions 11) also compete with other combinations (reaction 3).

$${\equiv}Si^{\bullet} + {\equiv}SiNH^{\bullet} \rightarrow HN(S{\equiv})_2 \qquad (11b)$$

$${\equiv}Si^{\bullet} + {}^{\bullet}N(Si{\equiv})_2 \rightarrow N(Si{\equiv})_3 \qquad (11c)$$

Reactions 10 and 11 lead to a consumption of the radicals which hinders the cross-linking of silicon atoms via Si–Si or Si–C–Si bridges, thus avoiding the formation of amorphous silicon carbide and allowing the complete amination of PCS.

It is not possible to state from our results whether the amination of the Si–C bonds involves radical substitution only or if nucleophilic substitution also takes place. In fact, both mechanisms might take place. An other interesting possibility is the intermediate formation of Si–H bonds,[38] followed by nucleophilic substitution:

$${\equiv}Si{-}R \rightarrow {\equiv}Si^{\bullet} + R^{\bullet} \quad (R = CH_3, CH_2{-}Si{\equiv}) \qquad (1)$$

$$Si^{\bullet} + NH_3 \rightarrow Si{-}H + {}^{\bullet}NH_2 \qquad (10a)$$

$${\equiv}Si{-}H + NH_3 \rightarrow {\equiv}Si{-}NH_2 + H_2 \qquad (7)$$

The comparison of the silicon loss in argon and in ammonia (Table I) shows that the loss of organosilicon species is noticeably lower under ammonia than under argon. This behavior may be explained by the early amination of Si–H bonds (reaction 7) to give $Si{-}NH_2$ groups which may then condense through transamination reactions (reactions 12), leading to a cross-linking of the chains by Si–N–Si bridges. These reactions are observed in the range 200–500 °C in the case of polysilazanes,[39,40] thus they may occur before the fragmentation reactions.

$$2{\equiv}Si{-}NH_2 \rightarrow {\equiv}Si{-}NH{-}Si{\equiv} + NH_3 \qquad (12a)$$

$$2{\equiv}Si{-}NH{-}Si{\equiv} \rightarrow N(Si{\equiv})_3 + {\equiv}Si{-}NH_2 \qquad (12b)$$

The removal of excess carbon from SiC and Si_3N_4 ceramic powders with ammonia has been recently investigated; it was shown that carbon is removed as HCN above 700 °C (reaction 13) and dissociation of ammonia was

$$C + NH_3 \rightarrow HCN + H_2 \qquad (13)$$

observed simultaneously.[10] The elemental analyses displayed in Table I shows that, even under our conditions, amination and carbon removal are nearly complete at 750 °C, which explains why the escape of HCN arising from reaction 14 is negligible in the case of PCS.

In conclusion, we have tried to give in this paper a complete and reasonable scheme of the reactions involved in the first steps of the pyrolysis of PCS. Under argon, simple radical reactions (homolytic cleavage of Si–H and Si–C bonds plus H abstraction) account both for the gases evolved (H_2, CH_4) and for the organosilicon fragments arising from the degradation of the polycarbosilane skeleton. The escape of hydrogen starts at the same temperature as the fragmentation; accordingly, cross-linking of PCS before fragmentation, by dehydrocoupling of the Si–H bonds, must be discarded. Under ammonia, nucleophilic substitution of Si–H bonds by ammonia first occurs; at higher temperatures, the substitution of Si–C bonds probably involves homolytic cleavages; however, in this case, H abstraction from N–H bonds hinders the cross-linking via Si–Si and Si–C–Si bridges, which allows complete amination.

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