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PHOTOCHLORINATION OF TETRAMETHYLSILANE AND HEXAMETHYLDISILANE IN THE GAS PHASE

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SUMMARY

Preliminary studies of the reaction of chlorine with tetramethylsilane and hexamethyldisilane in the gas phase show that the photochlorination of tetramethylsilane is complex, giving different products from the corresponding reaction in solution and having an explosion boundary. At pressures below the explosion boundary the main products are ethylene, hydrogen chloride, dimethylchlorosilane, and more highly chlorinated methylsilanes. Above the explosion boundary main products after explosion are methane, acetylene, ethylene, hydrogen chloride, and silicon tetrachloride. Hexamethyldisilane reacts rapidly with chlorine in the dark, as it does in solution, forming mainly trimethylchlorosilane along with similar products to those found with tetramethylsilane. Subsequent photochlorination of trimethylchlorosilane follows a similar course to that of tetramethylsilane in the gas phase. Tentative mechanisms involving "hot" molecules are suggested.

INTRODUCTION

There is a long-standing literature on the chlorination of methylsilanes, mainly concerned with establishing optimum conditions for the preparation of particular chlorosilanes required as precursors to

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organosiloxane polymers, with little attention to mechanistic detail.[1] Most work on the photolytic reaction of silanes with elementary chlorine has been done in dilute solution, photochemical reactions of chlorine with pure liquid or gaseous silanes having been reported to be complex, vigorous and occasionally explosive.[2] Even under mild conditions, several products are formed, but the essential features of chlorination in solution are clear. Thus, with tetramethylsilane the primary product of chlorination is chloromethyltrimethylsilane:

$$Me_4Si + Cl_2 \xrightarrow{h\nu} Me_3SiCH_2Cl + HCl$$

Further chlorination also occurs, giving both $Me_2Si(CH_2Cl)_2$ and $Me_3SiCHCl_2$ as principal products, with small quantities of products containing three chlorine atoms per molecule.[3,4] In contrast, photochemical chlorination of trimethylchlorosilane proceeds by exhaustive chlorination of one methyl group, forming $Me_2\overset{Cl}{Si}CH_2Cl$ and $Me_2\overset{Cl}{Si}CHCl_2$ as the main products.[4] Chlorination at silicon is not observed in the above reaction systems. Silicon hydrides are chlorinated very readily in solution,[5] even in the dark, forming silicon-chlorine bonds:

$$R_3SiH + Cl_2 \rightarrow R_3SiCl + HCl$$

Disilanes are also very readily chlorinated. Thus, hexamethyldisilane in carbon tetrachloride reacts vigorously with molecular chlorine at room temperature, with scission of the silicon-silicon bond to form trimethylchlorosilane.[6]

So far as we know, there is no literature on the gas-phase chlorination of organosilicon compounds, and very little on their gas-phase reaction with other halogens. Thermal iodination of tetramethylsilane proceeds very simply, giving only iodomethyltrimethylsilane and hydrogen iodide.[7] On the other hand, thermal iodination of hexamethyldisilane proceeds by a radical exchange reaction:[8]

$$Me_3SiSiMe_3 + I\cdot \rightarrow Me_3SiI + Me_3Si\cdot$$

and it appears that similar reactions may occur in the bromination of tetramethylsilane,[9] which gives significant amounts of dimethyldibromosilane as well as bromomethyltrimethylsilane. Silicon-bromine bonds are also formed in the bromination of hexamethyldisiloxane.[9] Radical exchange has been observed in the reactions of trifluoromethyl radicals with boron trimethyl and with Group IV tetramethyls, other than tetramethylsilane:[10]

$$\begin{aligned} Me_4M + \dot{C}F_3 &\rightarrow CF_3H + \dot{C}H_2MMe_3 \\ &\qquad [CF_3MMe_4] \rightarrow CF_3MMe_3 + Me\cdot \end{aligned}$$

Radical exchange between trifluoromethyl radicals and tetramethylsilane may have failed to occur because the reaction would be essentially thermoneutral; the corresponding reaction with chlorine atoms, on the other hand, would be strongly exothermic:

$$Cl\cdot + Me_4Si \rightarrow Me_3SiCl + Me\cdot$$

The simple, preliminary experiments described here were undertaken to find out to what extent photochlorination of organosilanes in the gas phase resembled or differed from photochlorination in solution, with particular reference to the possibility that radical exchange reactions at silicon occur in the gas phase. The silanes chosen were tetramethylsilane and hexamethyldisilane.

EXPERIMENTAL

Materials

Chlorine (Matheson) was dried by slow passage through a phosphorus pentoxide column and was kept free from hydrogen chloride by regular pumping from a pentane slush bath. Tetramethylsilane and hexamethyldisilane (Peninsular Chem. Research) were dried over molecular sieve. Methane (Matheson) was used without further purification. The purity of all materials was checked by mass spectrometry.

Apparatus

A conventional glass vacuum system was used, fitted with stainless steel valves throughout the storage and reaction regions of the apparatus. The cylindrical Suprasil reaction vessel, illuminated volume 178 cm^3, was embedded in a tubular furnace fitted with quartz end windows; temperature control was ±0.5°. The light source was a PEK 200 watt mercury arc from which the 3650 line was selected by broad band filters. Pressure measurement was with a quartz spiral gauge.

The reaction vessel was connected to the reactant supply manifold and to a mixing bulb. It was also connected to a Finnigan quadrupole mass spectrometer through a sampling system which consisted of a fine capillary reaching into the illuminated volume and connected to a 0.2 cm^3 standard volume from whence the sample could be directed to the mass spectrometer through a heated 3 mm diameter stainless steel tube by means of a stainless steel valve. The mass spectrometer was fitted with an adjustable leak.

The storage bulb, mixing bulb, and all connecting tubing were painted black, and the reaction vessel fitted with shutters, so that mixtures could be made up and admitted to the reaction vessel entirely in the dark.

The apparatus was tested by photolysing a mixture of methane (33.6 mmHg) and chlorine (14.4 mmHg) at 378 K. The photolysis proceeded smoothly, forming the expected photochlorination products: hydrogen chloride, methyl chloride, dichloromethane, chloroform, and carbon tetrachloride.

For quantitative mass spectrometry a peak height calibrant is necessary; silicon tetrafluoride, which has a convenient mass spectral peak at m/e 85^+ (SiF_3^+), was found to be suitable. Mixtures of silicon tetrafluoride and chlorine did not react in the dark, nor after prolonged photolysis, while added silicon tetrafluoride did not affect the photochlorination of methane.

During the chlorination experiments with tetramethylsilane and hexamethyldisilane, a film was deposited on the surface of the reaction vessel. This film was probably composed of polysiloxanes formed by the reaction of chlorosilanes with adsorbed water; in keeping with this conclusion, the film was resistant to acid but dissolved in hot aqueous sodium hydroxide.

RESULTS

[1] Chlorination of Tetramethylsilane

Gaseous mixtures of tetramethylsilane and chlorine were stable in the dark at 378 K, but reacted on photolysis. Initially the results appeared to be extremely inconsistent, but in due course the main reason for this was found to be the existence of an explosion boundary, with substantially different product composition on either side of the boundary. The explosion limits were not precisely determined, but mixtures in which the ratio of chlorine to tetramethylsilane ranged from 1.2:1 to 5.7:1 did not explode if the total pressure was between 40 and 80 mmHg. Mixtures of total pressure between 100 and 160 mmHg, with chlorine to tetramethylsilane ratios between 2.8:1 and 6:1, exploded immediately on photolysis, giving a sharp "pinging" sound, accompanied by a large pressure increase and by the deposition of a black solid. In one experiment with a chlorine to tetramethylsilane ratio of 2:1 and total pressure of 80 mmHg, steady reaction occurred on photolysis, but when the reaction cell was shuttered and a further 59 mmHg of chlorine added, explosion occurred on re-illumination of the cell. In a similar experiment with a chlorine to tetramethylsilane ratio of 2.9:1 and total pressure of 56 mmHg, no explosion was observed on adding a further 22.5 mmHg of chlorine, probably because the total pressure was only slightly above the limit and some depletion of reactants had occurred during the initial photolysis at the lower pressure. A few experiments were also done with added methane, with results described below. No experiments were done at total pressures outside the range of 40 to 160 mmHg.

Product analysis was by mass spectrometry, which enabled most of the products to be identified unambiguously. Mass spectrometry is, of course, particularly useful for the identification of chlorine-containing products, because of the distinctive doublets resulting from the Cl^{35} and Cl^{37} isotopes. In this paper, chlorine-containing ions in the mass spectrum will be identified by their m/e ratio corresponding to Cl^{35}, although in all cases higher mass peaks of the appropriate intensities attributable to Cl^{37} were also observed. The main mass spectral peaks observed in the "low pressure" region, where no explosion occurred, are in Table 1, while those in the "high pressure" region, after explosion, are in Table 2.

In the steady photolysis at "low pressure", product peaks could be observed to change regularly with time, while peaks characteristic of chlorine and tetramethylsilane declined (these were the molecule-ion 70^+ for chlorine and the base peak 73^+ for tetramethylsilane). Judged from relative intensities, hydrogen chloride and ethylene were the main products containing no silicon.

The mass spectra of methylsilicon compounds generally give very low intensity molecule-ions, but strong peaks corresponding to the loss of methyl from the molecule-ion. The assignments in Table 1 are made mainly on that basis, although molecule-ions were observed for methyltrichlorosilane and for silicon tetrachloride. The most intense silicon-containing ion was 79^+, while 93^+, 107^+, and 113^+ were of comparable intensity to each other, with 107^+ slightly the greatest. 133^+ was only observed when a large excess of chlorine was present. The best information on time-dependence of product formation came from the lowest pressure experiment at 40 mmHg. While 73^+ from tetramethylsilane decreased steadily, 79^+ rose rapidly then slowly decreased, as did 107^+ (which was always substantially smaller than 79^+); 113^+ grew relative to 107^+ later in the reaction.

Some test experiments had shown that photochlorination of methane proceeded normally in the apparatus, forming the expected range of products. When tetramethylsilane was added to a mixture of methane and chlorine which had been undergoing normal photolysis, the chlorine disappeared rapidly while photochlorination products of tetramethylsilane appeared. Mixtures of methane, tetramethylsilane, and chlorine

TABLE 1

Main Mass Spectral Peaks after Photolysis at "Low Pressure" (40-80 mmHg)

m/e	Ion	Product
28	$C_2H_4^+$	C_2H_4
29	$C_2H_5^+$	C_2H_5R
36	HCl^+	HCl
79	$MeSiHCl^+$	Me_2SiHCl
93	Me_2SiCl^+	Me_3SiCl and/or $EtMe_2SiCl$, Me_2SiHCl
107	$Me_2SiCH_2Cl^+$	Me_3SiCH_2Cl
	and/or $EtMeSiCl^+$	$EtMe_2SiCl$
113	$MeSiCl_2^+$	Me_2SiCl_2
133[a]	$SiCl_3^+$	$MeSiCl_3$

[a] Observed in an experiment with $Cl_2 : Me_4Si = 5.7:1$; not observed with lower $Cl_2 : Me_4Si$ ratios.

TABLE 2

Main Mass Spectral Peaks after Photo-Induced Explosion at "High Pressure" (100-160 mmHg)

m/e	Ion	Product
16	CH_4^+	CH_4
26	$C_2H_2^+$	C_2H_2
28	$C_2H_4^+$	C_2H_4
36	HCl^+	HCl
50	CH_3Cl^+	CH_3Cl
133	$SiCl_3^+$	$SiCl_4$
168	$SiCl_4^+$	$SiCl_4$

behaved like mixtures of tetramethylsilane and chlorine on photolysis, indicating that tetramethylsilane undergoes photochlorination at 105°C substantially faster than does methane.

[2] Chlorination of Hexamethyldisilane

Unlike tetramethylsilane, hexamethyldisilane reacted rapidly with chlorine in the dark, even at room temperature. The reaction was studied at 378 K, to minimise the risk of condensation of chlorosilicon products, with mixtures of chlorine and hexamethyldisilane in the total pressure range of 18 to 140 mmHg. The initial ratio of chlorine to hexamethyldisilane was varied between 0.9:1 and 13.6:1. In some further experiments chlorine was added to mixtures of hexamethyldisilane and methane, while in others successive quantities of chlorine were added to hexamethyldisilane.

In all of these experiments there was a rapid decrease in the 70^+ and 73^+ mass spectral peaks (characteristic of chlorine and hexamethyldisilane respectively) accompanied by the formation of trimethylchlorosilane, indicated by a prominent peak at 93^+. In most experiments the 70^+ peak disappeared completely and rapidly, even if the initial ratio of chlorine to hexamethyldisilane was high. The 70^+ peak was only observed in the later stages of those experiments in which successive quantities of chlorine had been added. It only appeared when no hexamethyldisilane remained, the system then consisting mainly of trimethylchlorosilane and chlorine. At this point, no further dark reaction occurred, but photochlorination of trimethylchlorosilane was observed when the reaction cell was illuminated. Naturally, photolysis of the other reaction mixtures in which all of the chlorine had been already consumed had no effect. In experiments with hexamethyldisilane, methane, and chlorine, no chlorination of methane occurred.

All four chlorosilanes, $Me_{(4-n)}SiCl_n$ $(n = 1\text{-}4)$, were formed in varying proportions depending on the initial ratios of reactants. Irrespective of the proportions of chlorine to hexamethyldisilane, trimethylchlorosilane was the major product, but the minor products depended on the conditions. With ratios of chlorine to hexamethyldisilane from ca. 1:1 to 6:1 the products were those listed in Table 3. The higher chlorosilanes became increasingly important as the initial proportion of chlorine was increased. Thus, when the initial ratio was lower than ca. 3:1 molecule-ions of both methyltrichlorosilane and silicon tetrachloride were observed, but with ratios above 3:1 silicon tetrachloride was the only product giving a 133^+ peak. With ratios of chlorine to hexamethyldisilane above 6:1 the additional products listed in Table 4 were also observed.

TABLE 3

Mass Spectral Peaks with $Cl_2 : Me_4Si \leqslant 6:1$

m/e	Ion	Product
16	$CH_4{}^+$	CH_4
26	$C_2H_2{}^{+\cdot}$	C_2H_2
36	HCl^+	HCl
93	Me_2SiCl^+	Me_3SiCl
133	$SiCl_3{}^+$	$SiCl_4$ and $MeSiCl_3$
148	$MeSiCl_3{}^+$	$MeSiCl_3$
168	$SiCl_4{}^{+\cdot}$	$SiCl_4$

TABLE 4

Additional Mass Spectral Peaks with $Cl_2 : Me_4Si > 6:1$

m/e	Ion	Product
28	$C_2H_4{}^+$	C_2H_4
99	$HSiCl_2{}^+$	$HMeSiCl_2$
113	$MeSiCl_2{}^+$	Me_2SiCl_2 and/or $HMeSiCl_2$
127	$ClCH_2SiMeCl^+$	$ClCH_2SiMe_2Cl$

Similar results to those summarised in Tables 3 and 4 were obtained in those experiments in which successive quantities of chlorine were added to hexamethyldisilane. At first, with a ratio of chlorine to hexamethyldisilane of 1:1, the products were those in Table 3. As further quantities of chlorine were added, corresponding successively to ratios of 3:1 and 5:1, the products in Table 4 were observed, the ratio of 93^+ to 133^+ dropping with each addition of chlorine. On further addition of chlorine, corresponding to a ratio of 9:1, excess chlorine was observed to be present and all of the hexamethyldisilane had been decomposed, mainly to trimethylchlorosilane. Photolysis then gave continued production of the products listed in Table 4 accompanied by a decrease in 93^+. This was in effect the photochlorination of trimethylchlorosilane.

Whilst addition of chlorine to mixtures of hexamethyldisilane and methane resulted only in the chlorination of hexamethyldisilane, the presence of methane significantly affected the ratio of 93^+ to 133^+, as shown in Table 5.

TABLE 5

Effect of Added Methane

$P_{Me_6Si_2}$/mmHg	P_{Cl_2}/mmHg	P_{CH_4}/mmHg	$[Cl_2]/[Me_6Si_2]$	$93^+/133^+$
20	120	0	6.0	1.6
15	87	19	5.8	5.8
6.2	84.5	29.5	13.6	3.0

As it has been shown that there is no dark reaction between methane and chlorine under these conditions, the effect in Table 5 strongly indicates that methane is acting as a third body in energy transfer from "hot" species.

DISCUSSION

[1] Chlorination of Tetramethylsilane

Whilst there is clearly insufficient quantitative information from these preliminary experiments to establish a reaction mechanism, some tentative conclusions can be drawn from the above results in the light of the known chemistry of related organosilicon compounds. The initial steps in the gas-phase photochlorination of tetramethylsilane are likely to be the same as in solution, viz.

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad [1]$$

$$Me_4Si + Cl\cdot \rightarrow Me_3Si\dot{C}H_2 + HCl \qquad [2]$$

$$Me_3Si\dot{C}H_2 + Cl_2 \rightarrow Me_3SiCH_2Cl + Cl\cdot \qquad [3]$$

Thereafter, the gaseous and liquid phase experiments proceed very differently. In the gas phase there is no evidence for further chlorination at carbon, which is such a clear feature of the experiments in solution. On the other hand, both silicon-hydrogen and silicon-chlorine bonds are formed in the gas phase, but not in solution. Photolysis can produce chlorine atoms with excess translational kinetic energy, but in our experiments with 3650 Å light, this excess would only be about 42 kJ per chlorine atom and in any case most of the chlorine atoms in the system would be produced without this excess energy in the chain propagation reaction [3]. Also, the temperature of our experiments, 378 K, was relatively low. Consequently, the most likely explanation for the extensive gas-phase conversion of tetramethylsilane to products not found in solution is that the exothermic reactions produced chemically-activated molecules in the gas-phase.

It is tempting to suggest that the expected radical exchange reaction occurred,

$$Me_4Si + Cl\cdot \rightarrow [Me_4SiCl] \rightarrow Me_3SiCl + Me\cdot \qquad [4]$$

This would be exothermic by about 167 kJ mol^{-1} and would account for the formation of silicon-chlorine bonds. However, it would imply the concomitant formation of substantial quantities of methane and methyl chloride, which were not detected (unless the high exothermicity resulted in "hot" methyl radicals leading directly to hydrogen chloride and hydrocarbons by reaction with chlorine). Also, there were no products characteristic of the chlorination of trimethylchlorosilane, which should have been distinctive, judging from the results in solution.[4] While reaction [4] may occur to a small extent, it is unlikely to be of major importance. Elimination of methylene, reaction [5], can be discounted as this reaction is not exothermic.

$$Me_3SiCH_2Cl \rightarrow Me_3SiCl + CH_2 \qquad [5]$$

A known reaction of chloromethyltrimethylsilane is rearrangement, reaction [6]:

$$Me_3SiCH_2Cl \rightarrow EtMe_2SiCl \qquad [6]$$

This reaction is catalysed by aluminium trichloride in the liquid phase,[11] but could occur in our experiments on the surface of the reaction vessel, or even homogeneously in the gas phase

(close up gap)

(there are precedents for gas-phase reactions in organosilicon chemistry following the same route as aluminium chloride-catalysed reactions in solution[12]). The carbon-chlorine bond dissociation energy in chloromethyltrimethylsilane may be taken to be the same as in simple alkyl chlorides, say 343 kJ mol^{-1}, while the silicon-chlorine bond dissociation energy is at least 523 kJ mol^{-1}. Accordingly, reaction [6] is exothermic by at least 180 kJ mol^{-1}, forming "hot" ethyldimethylchlorosilane. It is known[13] that the main decomposition route of "hot" ethylsilane is β-elimination:

$$EtSiH_3^* \rightarrow C_2H_4 + SiH_4$$

The corresponding reaction here is:

$$EtMe_2SiCl^* \rightarrow C_2H_4 + Me_2\underset{\displaystyle H}{\underset{|}{Si}}Cl \qquad [7]$$

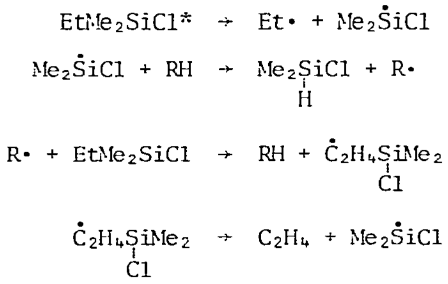
which neatly accounts for the observed formation of a major product containing a silicon-hydrogen bond, and for the striking fact that the main organic product of the photolysis is ethylene. The mass spectral peaks for the silicon-containing products are entirely consistent with the presence of ethyldimethylchlorosilane, as is the observation of a

29^+ peak (Table 1). Once dimethylchlorosilane has been formed, the formation of dimethyldichlorosilane is readily accounted for by the following well-known reactions:

$$\mathrm{Me_2SiHCl + Cl\cdot \rightarrow Me_2\dot{S}iCl + HCl} \qquad [8]$$

$$\mathrm{Me_2\dot{S}iCl + Cl_2 \rightarrow Me_2SiCl_2 + Cl\cdot} \qquad [9]$$

It should be noted that reaction [9] is very strongly exothermic, by at least 280 kJ $\mathrm{mol^{-1}}$. The alternative decomposition of "hot" ethyldimethylchlorosilane by a radical chain sequence, as in the pyrolysis of ethyltrimethylsilane and ethyltrichlorosilane,[14] would yield the same final products:



$$\mathrm{EtMe_2SiCl^* \rightarrow Et\cdot + Me_2\dot{S}iCl} \qquad [10]$$

$$\mathrm{Me_2\dot{S}iCl + RH \rightarrow Me_2\underset{H}{Si}Cl + R\cdot} \qquad [11]$$

$$\mathrm{R\cdot + EtMe_2SiCl \rightarrow RH + \dot{C}_2H_4\underset{Cl}{Si}Me_2} \qquad [12]$$

$$\mathrm{\dot{C}_2H_4\underset{Cl}{Si}Me_2 \rightarrow C_2H_4 + Me_2\dot{S}iCl} \qquad [13]$$

where R• is any radical.

Reactions [1]-[3], [6]-[9], possibly with [10]-[13], thus account for the strikingly distinctive range of products and for the observed time-dependence of the formation of these products. This scheme also accounts for the substantially different course followed by the chlorination in the gas phase as compared to the liquid phase. A similar sequence of reactions would account for the formation of methyltrichlorosilane in experiments with a high proportion of chlorine.

In experiments at "high pressure" where explosion occurred, there was total replacement of methyl at silicon by chlorine (in view of the relatively strong peaks at 168^+ due to silicon tetrachloride, the 133^+ peaks were probably $\mathrm{SiCl_3^+}$ ions from silicon tetrachloride rather than from methyltrichlorosilane), with the formation of substantial quantities of acetylene and methane. In these high pressure experiments the energy released from the exothermic reactions [6] and [9] may simply cause a thermal explosion and not a branched-chain explosion. The appearance of methane as a prominent product may well indicate that radical exchange does occur in this higher energy environment, either <u>via</u> reaction [4] or <u>via</u> a similar reaction involving the activated dimethyldichlorosilane formed in reaction [9].

$$Me_2SiCl_2^* + Cl\cdot \rightarrow [Me_2SiCl_3] \rightarrow MeSiCl_3 + Me\cdot \qquad [14]$$

Reaction [14] in turn, is also exothermic, by <u>ca</u>. 167 kJ. Acetylene could result from addition reactions between ethylene and chlorine followed by dehydrochlorination, but these suggestions can only be tentative at this stage.

Hence, gas-phase photochlorination of tetramethylsilane has been shown to proceed quite differently from the corresponding process in solution; several interesting reactions are involved, but there is no clear evidence that radical exchange occurs, except possibly with highly chemically-activated molecules. These reactions would repay further study, both in relation to mechanism and to synthetic utility.

[2] <u>Chlorination of Hexamethyldisilane</u>

Hexamethyldisilane reacted rapidly with chlorine in the dark, giving trimethylchlorosilane as the main product, as it does in solution.[6] However, it is evident from the product composition given in Tables 3 and 4 that the total mechanism in the gas phase is extremely complex. It is likely that the initial reaction is [15] and that the complexities result from the high degree of chemical activation imparted to trimethylchlorosilane in reaction [15], which is strongly exothermic.

$$Cl_2 + Me_3SiSiMe_3 \rightarrow 2Me_3SiCl^* \qquad [15]$$

The products listed in Table 3 are reminiscent of those formed in the explosive photochlorination of tetramethylsilane (Table 2), and it is extremely probable that chlorine atoms were present. In the dark these could arise from reactions such as [16] or [17], initiating an "energy chain".

$$Me_3SiCl^* + Cl_2 \rightarrow Me_3SiCl + 2Cl\cdot \qquad [16]$$

$$\searrow [Me_3SiCl_2]^* + Cl\cdot \qquad [17]$$

The energetics of reactions [15]-[17] cannot be reliably estimated because of the considerable uncertainty in the heat of formation of trimethylchlorosilane and in the silicon-chlorine bond dissociation energy, but for reactions [16] and [17] to occur the heat of formation of trimethylchlorosilane should be -375 kJ mol^{-1} or less. Literature values[15] range from -332 to -442 kJ mol^{-1}.

Trimethylchlorosilane could then be formed in three ways: (i) stabilisation of Me_3SiCl^* by collision:

$$Me_3SiCl^* + M \rightarrow Me_3SiCl + M \qquad [18],$$

(ii) from reaction [16], and (iii) from subsequent reaction of hexamethyldisilane with chlorine atoms:

$$Me_3SiSiMe_3 + Cl\cdot \rightarrow Me_3SiCl + Me_3Si\cdot \qquad [19]$$

$$Me_3Si\cdot + Cl_2 \rightarrow Me_3SiCl + Cl\cdot \qquad [20]$$

Reactions [19] and [20] are exactly analogous to the reactions of iodine with hexamethyldisilane.[8]

A further possibility is the reaction of Me_3SiCl^* with chlorine atoms, $Me_3SiCl^* + Cl\cdot \rightarrow [Me_3SiCl_2]^*$ [21] yielding an even more highly vibrationally excited intermediate than the initially "hot" trimethylchlorosilane from reaction [15]. These "hot" molecular species would then provide the high energy environment, analogous to the explosive photochlorination of tetramethylsilane, for the formation of the more highly chlorinated silanes and the hydrocarbons which were observed (Table 3), through a variety of radical reactions and molecular eliminations. Strong evidence for the participation of "hot" trimethylchlorosilane is provided by the experiments with added methane. It is clear from the $93^+/133^+$ ratios in Table 5 that methane suppresses the formation of more highly chlorinated products, even at high ratios of chlorine to hexamethyldisilane.

The stepwise addition of chlorine to hexamethyldisilane produced more controlled chlorination conditions and enabled unreacted chlorine to be observed, once all of the hexamethyldisilane had been consumed. Photolysis of the reaction mixture at this stage, which was in effect the photochlorination of trimethylchlorosilane, showed a similarity to the non-explosive photochlorination of tetramethylsilane (cf. Tables 1 and 4). As the trimethylchlorosilane was consumed, ethylene, methyldichlorosilane, and chloromethyldimethylchlorosilane were formed. These products may be accounted for by reactions [22]-[25], which are similar to reactions [2], [3], [6], and [7].

$$Me_3SiCl + Cl\cdot \rightarrow HCl + \dot{C}H_2SiMe_2Cl \qquad [22]$$

$$\dot{C}H_2SiMe_2Cl + Cl_2 \rightarrow ClCH_2SiMe_2Cl + Cl\cdot \qquad [23]$$

$$ClCH_2SiMe_2Cl \rightarrow EtSiMeCl_2{}^* \qquad [24]$$

$$EtSiMeCl_2{}^* \rightarrow C_2H_4 + HSiMeCl_2 \qquad [25]$$

Our experiments were no more than preliminary and certainly did not elucidate this extremely complex mechanism, but the above proposals should be regarded as representing reasonable speculation as to the overall features of the chlorination of hexamethyldisilane.

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