

The gas-phase reactions of SiCl₄ and Si₂Cl₆ with CH₃OH and C₂H₅OH: An investigation by mass spectrometry and matrix-isolation infrared spectroscopy

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The gas phase reactions of SiCl₄ and Si₂Cl₆ with CH₃OH and C₂H₅OH have been investigated using both mass spectrometry and matrix isolation techniques. SiCl₄ reacts with both CH₃OH and C₂H₅OH upon mixing of the vapours for times in excess of 3 h to generate the HCl-elimination products SiCl₃OR (R = CH₃ or C₂H₅). The identity of these products is confirmed by deuteration experiments and by *ab initio* calculations at the HF/6-31G(d) level. Further products are generated when the mixture is passed through a tube heated to 750 °C. Si₂Cl₆ reacts with CH₃OH and C₂H₅OH *via* a different mechanism in which the Si–Si bond is cleaved to yield SiCl₃OR and HCl. Other products of the type SiCl_{4–n}(OCH₃)_n are tentatively identified by a combination of mass spectrometric and matrix isolation measurements. These latter products indicate further replacement of Cl atoms by OR groups as a result of reaction of CH₃OH or C₂H₅OH with the initial product.

Introduction

The alcoholysis of chlorosilanes has for many years been an important process in the manufacture of organosilicon reagents for the chemical industry.¹ More than 50 years ago partial hydrolysis reactions of SiCl₄ were carried out in order to generate a homologous series of silicon oxychlorides of general formula Si_nO_{n–1}Cl_{2n+2}.^{2,3} This work was soon extended to investigate the interaction of alcohols with SiCl₄.^{4,5} By this time a wide range of alkyl chlorosilicates of the type Si(OR)_nCl_{4–n} had been prepared and characterised. Such compounds are important synthetically because further hydrolysis causes replacement of the Cl atoms without simultaneous replacement of the alkoxy groups to give polymeric species of the type [SiO(OR)₂]_n.⁴

In recent times an impetus has been given to work involving silicon oxychloride species by the importance of the combustion reaction of SiCl₄ in O₂ to give SiO₂.⁶ This reaction is used in chemical vapour deposition (CVD) and chemical vapour transport (CVT) processes and there has been interest in the reaction mechanism. A recent theoretical study has suggested that the reaction proceeds *via* a chlorosiloxane ring (Cl₂SiO)₂.⁷ Also connected with the use of SiCl₄ in CVD and CVT processes is the need to obtain this reagent in a high degree of purity. As such there is a need to develop a greater understanding of the reactions of SiCl₄ and the role of silicon oxychlorides—as may be illustrated by the photochemical synthesis and determination by infrared spectroscopy of trichlorosilanol SiCl₃OH in SiCl₄.^{8,9}

Matrix isolation is an established method to study reaction intermediates and mechanism.¹⁰ Many silicon compounds have been investigated using this approach but there is only

limited information on the hydrolysis or alcoholysis reactions of silicon tetrahalides. Ault has shown¹¹ that SiF₄ forms 1:1 complexes with H₂O, CH₃OH and CH₃OCH₃ when the individual reagents are condensed by twin-jet deposition onto a cold CsI window with excess argon. Use of a merged-jet deposition arrangement did not significantly increase the yield of these species suggesting that they do not exist at appreciable concentration in the gas phase but rather are formed on the surface of the matrix during deposition. There was no sign of HF elimination from these adducts, reflecting most probably the strength of the Si–F bonds. By contrast codeposition of SiCl₄ and CH₃OH in twin- or merged-jet mode led to no identifiable product bands in the condensate.¹² HSiCl₃ does, however, form the HCl-elimination product Cl₂HSiOCH₃ upon codeposition with SiCl₄ by twin-jet or merged-jet methods.¹² In this case the yield of product is increased significantly on switching to merged-jet mode suggesting that a gas-phase reaction does occur. The authors of this work were surprised to find that SiCl₄ did not show similar reactivity to that of HSiCl₃. TiCl₄ reacts with CH₃OH under these conditions.¹³ In twin-jet mode the principal product is the 1:1 adduct TiCl₄·CH₃OH but this gives way to the HCl-elimination product TiCl₃OCH₃ when merged-jet mode is used to deposit the matrix. Heating of the merged-jet region leads to destruction of TiCl₃OCH₃ and the formation of a secondary product presumably by elimination of CH₃Cl.

The initial aim of the research presented here was to reinvestigate the SiCl₄ + CH₃OH reaction using the techniques of mass spectrometry and matrix-isolation infrared spectroscopy. It was thought that the use of longer mixing times might allow products to form *via* a gas-phase equilibrium, and in order to obtain a more complete picture, combinations of ethanol,

methanol, Si_2Cl_6 and SiCl_4 were studied. In the case of Si_2Cl_6 , one point of interest was whether Si–Si bond rupture would compete with HCl elimination in the formation of products.

Experimental

Mass spectrometric studies were carried out at Southampton using a VG mass lab-automated MS quadrupole instrument operating with an ionisation energy of *ca.* 70 eV and controlled by a PC. The matrix-isolation equipment used at Reading¹⁴ or Southampton¹⁵ has been described in detail elsewhere. High purity nitrogen and argon (BOC 99.999%) were employed as matrix gases in the IR studies and deposition times were typically 10–30 min. During this period the central CsI window was maintained at *ca.* 12 K, and spectra were recorded using a PE 983G spectrometer interfaced with a data station. A typical resolution and accuracy of $\pm 2 \text{ cm}^{-1}$ or better was achieved.

Samples of SiCl_4 (99% purity), Si_2Cl_6 (96% purity), CH_3OH (99.9% purity) and $\text{C}_2\text{H}_5\text{OH}$ (99.9% purity) were supplied by Aldrich and further purified on a vacuum line by distillation and by the freeze–pump–thaw process. This ensured the removal of water and dissolved oxygen from the alcohol samples. Gas mixtures were made up on a standard vacuum line using manometric measurements and vapour pressure data to control the composition of the mixture. Gaseous samples were allowed to mix before deposition onto the cold window *via* a needle valve. Where appropriate the deposition tube was heated by a spirally-wound resistance wire whose current was controlled by a variac. Temperatures were controlled to $\pm 5^\circ\text{C}$ over a length of 25 cm of tube.

Structural modelling was carried out at the HF/6-31G(d) level, and vibrational frequency calculations were performed using the Gaussian 98 software package.^{16a} Calculated vibrational frequencies were scaled by 0.8929 as is standard for the Hartree–Fock method.^{16b}

Results and discussion

Reaction of SiCl_4 with methanol

In the initial experiments, a gas phase mixture was made up consisting of 1 Torr of SiCl_4 and 1 Torr of CH_3OH , and the reagents were allowed to mix at room temperature for a period of 3 h before being admitted into the mass spectrometer. The mass spectrum showed prominent peaks arising from the

following ions (*m/z* values for the most abundant isotopomer are given in parentheses): SiCl_4^+ (170), SiCl_3^+ (135), SiCl_2^+ (98), SiCl^+ (63), $\text{SiCl}_3\text{OCH}_3^+$ (166), $\text{SiCl}_2\text{OCH}_3^+$ (129), SiClOCH_3^+ (94) and HCl^+ (36), and a typical spectrum is illustrated in Fig. 1. These observations provide a body of evidence for the formation of the HCl elimination product $\text{SiCl}_3\text{OCH}_3$. This reaction is analogous to the formation of $\text{TiCl}_3\text{OCH}_3$, which has been reported when TiCl_4 and CH_3OH are reacted in a merged-jet system.¹³

When the experiment was repeated but with the reagents being flowed together into the mass spectrometer through a merged-jet system, rather than being premixed, only peaks due to the reactants were seen, namely those arising from the ions: SiCl_4^+ (170), SiCl_3^+ (135), SiCl_2^+ (98), SiCl^+ (63), CH_3OH^+ (32), CH_3O^+ (31), CH_2O^+ (30), CHO^+ (29) and CH_3^+ (15). This shows that no reaction takes place and demonstrates that SiCl_4 is less reactive than TiCl_4 under these conditions in line with the previous observations of Brehm, Ault and Everhart.^{13,14}

When a premixed (mixing time = 3 h) gaseous sample of SiCl_4 (1 Torr) and CH_3OH (1 Torr) was passed through a tube heated to 630°C , prior to entering the mass spectrometer, ions resulting from the product $\text{SiCl}_3\text{OCH}_3$ were not seen, but a pair of peaks at *m/z* = 50 and 52 in a 3:1 intensity ratio were seen, alongside features due to SiCl_4 and CH_3OH fragmentation. It is likely that these peaks arise from the molecular ion of CH_3Cl , suggesting that $\text{SiCl}_3\text{OCH}_3$ may decompose thermally to eliminate CH_3Cl in a manner similar to the thermal decomposition of $\text{TiCl}_3\text{OCH}_3$.¹³

The reaction was then investigated using matrix-isolation infrared spectroscopy (N.B. argon replaced dinitrogen in some matrix isolation experiments but in control experiments we could find no difference in behaviour when these two matrix gases were interchanged). As before, blank experiments were conducted on both individual reagents (SiCl_4 (1 Torr) in Ar (100 Torr) and CH_3OH (1 Torr) in Ar (100 Torr)) before any codeposition experiments were conducted. The spectra obtained from these reagents were in good agreement with literature spectra.^{17,18} When both reagents were codeposited onto the cold matrix window using merged-jet mode without premixing only bands of the unreacted reagents were seen. However, when the reaction was repeated allowing the gaseous reagents to mix for 3 h before deposition new bands of a reaction product, alongside the band of HCl at 2530 cm^{-1} , were clearly seen. The position of the HCl stretching frequency suggests that this molecule exists as the $\text{CH}_3\text{OH} \cdots \text{ClH}$ complex.¹²

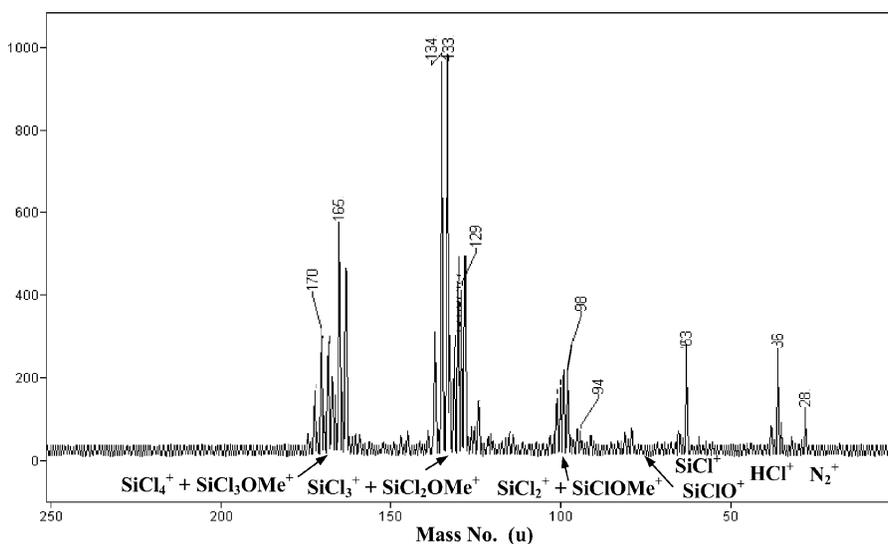


Fig. 1 Mass spectrum of the products of the gas phase reaction of SiCl_4 (1 Torr) with CH_3OH (1 Torr). The reagents have been mixed for 3 h at room temperature prior to being admitted to the mass spectrometer.

The bands of these products are listed in Table 1. It is likely that the product formed alongside HCl is $\text{SiCl}_3\text{OCH}_3$ whose formation in this reaction was suggested by mass spectrometry.

In order to help confirm this hypothesis the experiment was repeated using CD_3OD in place of CH_3OH and the shifts of the product band positions upon deuteration were noted. Finally the experimentally observed frequencies for both the H- and D-containing products were compared with those calculated at the HF/6-31G(d) level for $\text{SiCl}_3\text{OCH}_3$ and $\text{SiCl}_3\text{OCD}_3$. The observed and calculated frequencies are listed in Table 1 where approximate descriptions of the vibrations giving rise to the bands are given. These assignments are based on the results of the calculations and on the known regions of absorption of vibrational modes. The product shows bands entirely characteristic of the CH_3O - moiety together with strongly-coupled $\nu(\text{Si-O})$ and $\nu(\text{C-O})$ modes. It may be noted that the band assigned to $\nu(\text{C-O})$ (1100 cm^{-1} in the $\text{SiCl}_3\text{OCH}_3$ product) is at a much higher frequency than the corresponding band of methanol (1034 cm^{-1})¹⁷ and shifts to high frequency upon deuteration. Both observations are indicative of strong coupling not only to $\nu(\text{Si-O})$ but also to C-H deformation modes.¹² The product shows only one infrared active $\nu(\text{Si-Cl})$ stretch at 600 cm^{-1} . Two such bands ($A_1 + E$), separated by an appreciable energy gap ($\nu_E > \nu_{A1}$) would be expected from the local C_{3v} symmetry of the SiCl_3 moiety, but comparison with related systems shows that the E mode is significantly more intense in the infrared than the A_1 mode. Examples of similar XYZ₃ molecules include HSiCl_3 (573 and 513 cm^{-1}),¹² FSiCl_3 (640 and 465 cm^{-1}),¹⁹ HGCl_3 (709 and 418 cm^{-1}),²⁰ OPCl_3 (581 and 486 cm^{-1})²¹ and SPCl_3 (542 and 435 cm^{-1}).²² It is likely, therefore that the band we observe here arises from the degenerate antisymmetric stretch while the symmetric stretch occurs at lower frequency, is of lesser intensity, and is not detected. For $\text{SiCl}_3\text{OCH}_3$ $\nu_{\text{asym}}(\text{SiCl}_3)$ (A_1) is calculated to occur at 573 cm^{-1} . The failure to observe a band arising from this vibration in our experiments probably results from lack of intensity. The observed shifts in band position upon deuteration and the close correlation between observed and calculated spectra leave little doubt that the product generated here is $\text{SiCl}_3\text{OCH}_3$.

Our observations on $\text{SiCl}_3\text{OCH}_3$ are reminiscent of the findings of Ault and Everhart on the analogous species $\text{TiCl}_3\text{OCH}_3$ formed by reaction of TiCl_4 and CH_3OH in a merged-jet system.¹³ In this work, just one $\nu(\text{Ti-Cl})$ mode was observed (at 486 cm^{-1}), and a band at 1152 cm^{-1} was

assigned to $\nu(\text{C-O})$ which was similarly seen to shift to high frequency upon perdeuteration of the product.

Experiments were then carried out in which a gaseous mixture of SiCl_4 , CH_3OH and Ar were flowed through a heated pyrolysis tube at 350 or 750°C prior to condensation on the cold window. At 350°C no changes to the product spectrum were observed *i.e.* alongside bands of SiCl_4 and CH_3OH only those of $\text{SiCl}_3\text{OCH}_3$ and HCl were seen. The tube was then heated to 750°C . In this case weak new features were seen at 1439 , 1304 , 947 , 662 , 623 , 618 and 612 cm^{-1} . This suggests the formation of one or more Si-Cl-containing products. Unfortunately these products could be obtained neither in sufficient quantity nor purity to make identification possible. It is noteworthy that no CH_3Cl was seen as a product in these matrix experiments.²³ In the reaction of TiCl_4 and CH_3OH similar pyrolysis experiments were performed.¹³ Above 250°C $\text{TiCl}_3\text{OCH}_3$ was destroyed and CH_3Cl ^{13,23} was formed. It is clear that $\text{SiCl}_3\text{OCH}_3$ is more thermally stable than is $\text{TiCl}_3\text{OCH}_3$ and that, while some decomposes to give CH_3Cl (as shown by mass spectrometry) other decomposition pathways exist.

In order to explore this reaction further a range of mixing times (5 , 20 and 30 min) were employed. As the mixing time was increased the product concentration also increased but no new products were seen. The maximum product concentration was achieved after 3 h mixing. Prolonging the mixing time to 18 h did not cause any new product to appear. Accordingly, a mixing time of 3 h was used for all reactions of methanol with SiCl_4 . In all reactions a $1:1$ ratio of reactants was used. Experiments were also performed in which the matrix-isolated products were irradiated using the quartz-filtered, broad-band output ($\lambda \geq 190\text{ nm}$) of a medium-pressure mercury lamp. No change to the spectrum was observed under these conditions. This is expected, given that matrix-cage effects would inhibit dissociation of the isolated product molecules.

Reaction of SiCl_4 with ethanol

Mass spectrometric measurements were then made on gaseous samples of SiCl_4 (1 Torr) and $\text{C}_2\text{H}_5\text{OH}$ (1 Torr) which had been mixed for 18 h. It was found that much longer mixing times (18 versus 3 h) were required when ethanol replaced methanol as a reactant to build up a substantial concentration of product. The mass spectrum of such a mixture showed clear features assigned to $\text{SiCl}_3\text{OC}_2\text{H}_5^+$ (180), $\text{SiCl}_3\text{OCH}_2^+$ (165), $\text{SiCl}_2\text{CH}_2^+$ (128), SiCl_2OH^+ (115) and HCl^+ (36). The mass spectrum is illustrated in Fig. 2. This suggests that the HCl-elimination product has again been formed, in this case $\text{SiCl}_3\text{OC}_2\text{H}_5$. Matrix isolation experiments on gaseous samples of SiCl_4 (1 Torr), $\text{C}_2\text{H}_5\text{OH}$ (1 Torr) and Ar or N_2 (200 Torr) which had been mixed for 18 h support this assertion. The observed bands which are assigned to $\text{SiCl}_3\text{OC}_2\text{H}_5$ are listed in Table 2, where they are compared with calculated frequencies for the same species. The close correlation between observed and calculated spectra leaves little doubt that the product here is $\text{SiCl}_3\text{OC}_2\text{H}_5$.

Reactions of Si_2Cl_6 with methanol and ethanol

The next stage of the work was to investigate the reaction of Si_2Cl_6 with methanol and ethanol under similar conditions. The mass spectrum of Si_2Cl_6 has been discussed elsewhere.^{24,25} When a gaseous mixture of Si_2Cl_6 (1 Torr) and CH_3OH (1 Torr) was mixed for 3 h then flowed into the mass spectrometer, peaks were seen in the mass spectrum which were assigned to the ions: $\text{Si}(\text{OCH}_3)_3\text{Cl}^+$ (156), $\text{Si}(\text{OCH}_3)_2\text{Cl}_2^+$ (129), $\text{Si}(\text{OCH}_3)_2\text{Cl}^+$ (125), $\text{Si}(\text{OCH}_3)_3^+$ (121), $\text{Si}(\text{OCH}_3)\text{Cl}^+$ (94), $\text{Si}(\text{OCH}_3)_2^+$ (90), SiCl^+ (63), SiOCH_3^+ (59) and HCl^+ (36). This result is indicative of the formation of the products $\text{SiCl}_{4-n}(\text{OCH}_3)_n$ (where $n = 1-3$). No new peaks were seen at

Table 1 Observed and calculated frequencies of infrared absorption for the products formed by the gas-phase reaction of SiCl_4 with CH_3OH or CD_3OD on mixing for 3 h at room temperature. The compounds have been isolated in an argon matrix at 12 K at approximately a $1:100$ dilution

ν/cm^{-1} obs	ν/cm^{-1} calc ^a	ν/cm^{-1} obs	ν/cm^{-1} calc ^a	Approximate description
$\text{SiCl}_3\text{OCH}_3$	$\text{SiCl}_3\text{OCH}_3$	$\text{SiCl}_3\text{OCD}_3$	$\text{SiCl}_3\text{OCD}_3$	
2960	2956	2244	2217	$\nu(\text{C-H})$
2900	2889	2077	2069	$\nu(\text{C-H})$
2859	—	2143	—	$\nu(\text{H-Cl})^b$
1464	1463	1068	1067	$\delta(\text{CH}_3)^c$
1192	1182	1076	1102	$\nu(\text{Si-O})^c$
1108	1108	1128	1124	$\nu(\text{Si-O})^c$
815	774	781	742	$\delta(\text{Si-O-C})^c$
600	600	597	597	$\nu_{\text{asym}}(\text{SiCl}_3)$
^d	573	^d	573	$\nu_{\text{sym}}(\text{SiCl}_3)$

^a Calculated frequencies scaled by 0.8929 (see text). ^b $\nu(\text{H-Cl})$ of HCl (DCl) product. No products other than $\text{SiCl}_3\text{OCH}(\text{D})_3$ and $\text{H}(\text{D})\text{Cl}$ were seen in these experiments. ^c Significant coupling of vibrations occurs in this region. ^d Too weak to be observed (see text).

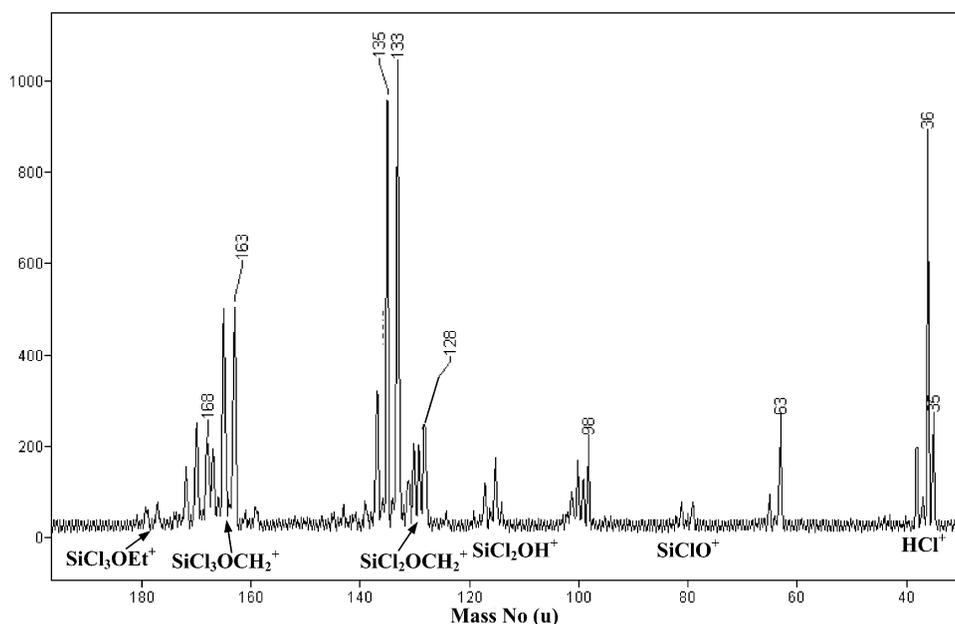


Fig. 2 Mass spectrum of the products of the gas phase reaction of SiCl_4 (1 Torr) with $\text{C}_2\text{H}_5\text{OH}$ (1 Torr). The reagents have been mixed for 18 h at room temperature prior to being admitted to the mass spectrometer.

higher mass, suggesting that products of formula $\text{Si}_2\text{Cl}_{6-n}(\text{OCH}_3)_n$ were not formed.

The reaction was then investigated by matrix-isolation infrared spectroscopy. Infrared spectra were recorded on condensed gaseous mixtures of Si_2Cl_6 (1 Torr), CH_3OH (1 Torr) and Ar (200 Torr) and of Si_2Cl_6 (1 Torr), CD_3OD (1 Torr) and Ar (200 Torr). The product bands observed in each case are listed in Table 3 and the spectra observed in the CH_3OH reaction are illustrated in Fig. 3. A comparison of the positions of these bands with those observed in the earlier experiments utilising SiCl_4 as a reactant demonstrates that the molecules $\text{SiCl}_3\text{OCH}_3$ and $\text{SiCl}_3\text{OCD}_3$ have been formed alongside HCl and DCl respectively. There is no unequivocal evidence for the formation of more substituted species in these spectra. However, bands are clearly seen (when CH_3OH is the reactant) at 3005, 2915, 1339 and 631 cm^{-1} which do not belong to $\text{SiCl}_3\text{OCH}_3$ and are not seen when SiCl_4 was reacted with CH_3OH . When CD_3OD was used as the reactant with Si_2Cl_6 in place of CH_3OH a number of weak features which probably

arise from more substituted products were seen. These features are listed in Table 3.

In a final series of experiments premixed gaseous samples (mixing time = 18 h) of Si_2Cl_6 (1 Torr), $\text{C}_2\text{H}_5\text{OH}$ (1 Torr) and N_2 or Ar (200 Torr) were studied by matrix isolation infrared spectroscopy. The observed bands are listed in Table 4 and the spectrum is illustrated in Fig. 4. A comparison of these bands with those seen when SiCl_4 and $\text{C}_2\text{H}_5\text{OH}$ are reacted together shows that $\text{SiCl}_3\text{OC}_2\text{H}_5$ has been formed. A number of additional bands were seen in the spectrum obtained when Si_2Cl_6 was reacted with $\text{C}_2\text{H}_5\text{OH}$ which were not seen when SiCl_4 was the reactant. The positions of these bands are listed

Table 2 Observed and calculated frequencies of infrared absorption for the molecule $\text{SiCl}_3\text{OC}_2\text{H}_5$ formed by the gas phase reaction of SiCl_4 and $\text{C}_2\text{H}_5\text{OH}$ on mixing for 18 h at room temperature. The compound has been isolated in an argon matrix at 12 K at approximately a 1:100 dilution

$\text{SiCl}_3\text{OC}_2\text{H}_5$ obs ν/cm^{-1}	$\text{SiCl}_3\text{OC}_2\text{H}_5$ calc ^a ν/cm^{-1}	Approximate description
2941	2951	$\nu(\text{C-H})$
2844	—	$\nu(\text{H-Cl})^b$
1446	1453	$\delta(\text{CH}_3)^c$
1393	1380	$\delta(\text{CH}_3)^c$
1172	—	$\nu(\text{C-O})^c$
1103	1101	$\nu(\text{C-O})^c$
1085	1085	$\nu(\text{Si-O})^c$
985	946	$\nu(\text{C-C})^c$
779	751	$\delta(\text{C-C-O})^c$
600	595	$\nu_{\text{asym}}(\text{SiCl}_3)$
^d	572	$\nu_{\text{sym}}(\text{SiCl}_3)$

^a Calculated frequencies scaled by 0.8929 (see text). ^b Band of HCl product. ^c Significant coupling of vibrations occurs in this region. ^d Too weak to be observed (see text).

Table 3 Observed infrared bands of the products of the gas phase reaction of Si_2Cl_6 with CH_3OH and CD_3OD on mixing for 3 h at room temperature. The products have been isolated in an argon matrix at 12 K at approximately a 1:100 dilution. The positions of the bands are compared with those of the matrix-isolated compound $\text{SiCl}_3\text{OCH}(\text{D})_3$ formed by the gas phase reaction of SiCl_4 with CH_3OH or CD_3OD

$\text{Si}_2\text{Cl}_6 + \text{CH}_3\text{OH}$ ν/cm^{-1}	$\text{SiCl}_4 + \text{CH}_3\text{OH}$ ν/cm^{-1}	$\text{Si}_2\text{Cl}_6 + \text{CD}_3\text{OD}$ ν/cm^{-1}	$\text{SiCl}_4 + \text{CD}_3\text{OD}$ ν/cm^{-1}	Approximate description
3005	—	—	—	$\nu(\text{C-H})^a$
2958	2960	2245	2244	$\nu(\text{C-H})^b$
2915	2900	2078	2077	$\nu(\text{C-H})^b$
2859	2859	2143	2143	$\nu(\text{H-Cl})^c$
2845	—	—	—	$\nu(\text{C-H})^a$
1464	1464	1062	1068	$\delta(\text{CH}_3)^b$
1339	—	1096	—	$\delta(\text{CH}_3)^a$
1189	1192	^d	1076	$\nu(\text{Si-O})^{b,e}$
1096	1100	1128	1128	$\nu(\text{C-O})^{b,e}$
1032	—	913	—	$\nu(\text{C-O})^{a,e}$
811	815	780	781	$\delta(\text{Si-O-C})^{b,e}$
—	—	665	—	$\nu(\text{Si-Cl})^a$
631	—	631	—	$\nu(\text{Si-Cl})^a$
600	600	600	600	$\nu(\text{Si-Cl})^b$

^a Band of unknown product, probably formed by replacement of Cl atoms by $\text{OCH}(\text{D})_3$ groups. These products are only formed when Si_2Cl_6 reacts with $\text{CH}(\text{D})_3\text{OH}(\text{D})$ and not when SiCl_4 reacts with the same alcohols. ^b Band of $\text{SiCl}_3\text{OCH}(\text{D})_3$. ^c Band of HCl. ^d Band not observed. ^e Significant coupling of vibrations occurs in this region.

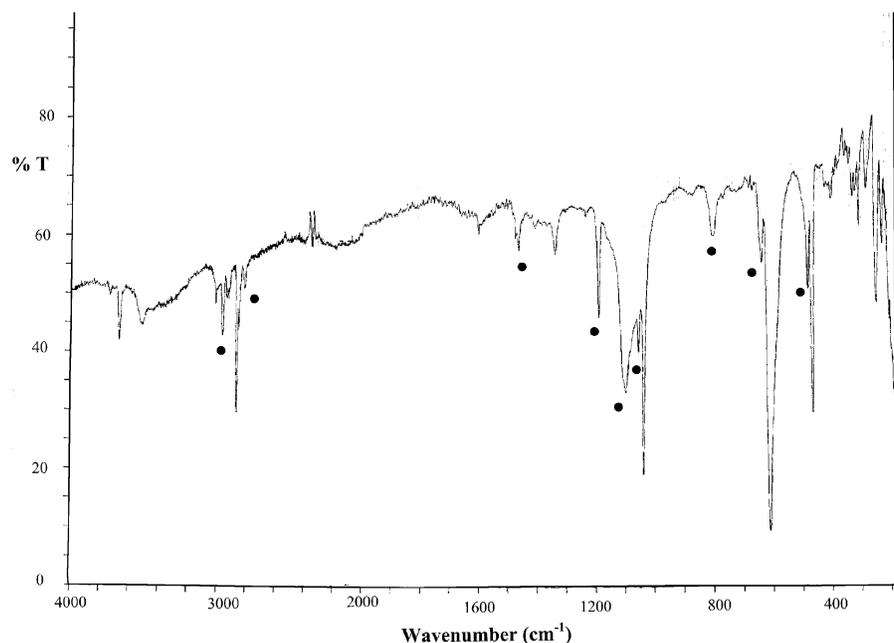


Fig. 3 Infrared spectrum (200–4000 cm^{-1}) of a low-temperature matrix (12 K) generated by condensing the products of the gas phase reagents Si_2Cl_6 (1 Torr), CH_3OH (1 Torr) and Ar (200 Torr). The reagents were mixed at room temperature for 3 h prior to deposition. Bands of the species $\text{SiCl}_3\text{OCH}_3$, which is also formed when SiCl_4 reacts under similar conditions with CH_3OH , are identified by the symbol ●.

in Table 4. It is likely that these bands arise from further substitution products.

Discussion

The mass spectrometric and matrix-isolation infrared spectroscopic data show that SiCl_4 reacts with CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ to give the HCl-elimination product SiCl_3OR ($\text{R} = \text{CH}_3$ or C_2H_5):

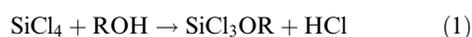


Table 4 Observed infrared bands of the products of the gas phase reaction of Si_2Cl_6 with $\text{C}_2\text{H}_5\text{OH}$ on mixing for 18 h at room temperature. The products have been isolated in an argon matrix at 12 K at approximately a 1:100 dilution. The positions of the bands are compared with those of the matrix-isolated compound $\text{SiCl}_3\text{OC}_2\text{H}_5$ formed by the gas phase reaction of SiCl_4 with $\text{C}_2\text{H}_5\text{OH}$

$\text{Si}_2\text{Cl}_6 + \text{C}_2\text{H}_5\text{OH}$ ν/cm^{-1}	$\text{SiCl}_4 + \text{C}_2\text{H}_5\text{OH}$ ν/cm^{-1}	Approximate description
2941	2951	$\nu(\text{C-H})^a$
2844	2844	$\nu(\text{H-Cl})^b$
1480		$\nu(\text{H-Cl})^c$
1445	1446	$\delta(\text{CH}_3)^{a,d}$
1394	1393	$\delta(\text{CH}_3)^{a,d}$
1171	1172	$\nu(\text{Si-O})^{a,d}$
^e	1103	$\nu(\text{C-O})^{a,d}$
1082	1085	$\nu(\text{C-O})^{a,d}$
1026		$\nu(\text{C-O})^{c,d}$
980	985	$\nu(\text{C-C})^{a,d}$
887		$\nu(\text{C-C})^{c,d}$
767	779	$\delta(\text{C-C-O})^{a,d}$
662		$\nu(\text{Si-Cl})^c$
631		$\nu(\text{Si-Cl})^c$
595	600	$\nu(\text{Si-Cl})^a$
485		$\nu(\text{Si-Cl})^c$

^a Band of $\text{SiCl}_3\text{OC}_2\text{H}_5$. ^b Band of HCl. ^c Band of unknown product, probably formed by replacement of Cl atoms by OC_2H_5 groups. These products are only formed when Si_2Cl_6 reacts with $\text{C}_2\text{H}_5\text{OH}$ and not when SiCl_4 reacts with the same alcohols. ^d Significant coupling of vibrations occurs in this region. ^e Band not observed.

This is a thermodynamically favourable process. Our HF 6-31G(d) calculations give values of $\Delta G_{\text{rxn}}^\circ = -43.5 \text{ kJ mol}^{-1}$ and $K_{\text{eq}} = 4.2 \times 10^7$ for the reaction. Our findings are similar to the observations of Ault and Everhart on the reaction of TiCl_4 and CH_3OH .¹³ The reaction of SiCl_4 and CH_3OH is, however, slower, as demonstrated by the observation that, unlike with TiCl_4 and CH_3OH , the product is not formed in a merged-jet system. The differences between these systems probably reflect the fact that the Ti–Cl bond in TiCl_4 is both longer (2.185 Å) and weaker (dissociation enthalpy, $\text{DH} = 345 \text{ kJ mol}^{-1}$)^{26†} than the Si–Cl bond in SiCl_4 (2.017 Å, 462 kJ mol^{-1})^{27†}. The HCl-elimination product is presumably formed *via* an adduct $\text{SiCl}_4\cdot\text{ROH}$ ($\text{R} = \text{CH}_3$ or $\text{C}_2\text{H}_5\text{OH}$). The analogous adduct $\text{SiF}_4\cdot\text{CH}_3\text{OH}$ is formed on deposition of SiF_4 with CH_3OH , although it does not eliminate HF.¹¹ The differences between our system and this are understandable. Fluorine is well known to stabilise higher coordination complexes of silicon relative to chlorine and therefore the lack of direct observation of $\text{SiCl}_4\cdot\text{ROH}$ is not surprising. On the other hand HCl elimination (from a more weakly bound complex) is more likely than HF elimination due to the weaker Si–Cl bond relative to the extremely strong Si–F [$\text{DH}(\text{SiF}_3\text{–F}) = 697 \text{ kJ mol}^{-1}$, $\text{DH}(\text{SiCl}_3\text{–Cl}) = 462 \text{ kJ mol}^{-1}$].²⁷ It is interesting to note that the principal products formed when Si_2Cl_6 reacts with CH_3OH or $\text{C}_2\text{H}_5\text{OH}$ are $\text{SiCl}_3\text{OCH}_3$ and $\text{SiCl}_3\text{OC}_2\text{H}_5$ respectively. This suggests that the major pathway for reaction of Si_2Cl_6 is *via* Si–Si bond breaking:-



where $\text{R} = \text{CH}_3$ or C_2H_5 . The difficulty with this pathway is that there was no evidence for formation of HSiCl_3 . Obviously some fragmentation peaks from HSiCl_3 in the mass spectra would be difficult to distinguish from those of Si_2Cl_6 . However we do not see any features arising from HSiCl_3 in any of our infrared spectra either.¹² It is, of course, possible that HSiCl_3 , if it were produced, would itself react with CH_3OH . It is

† DH values obtained *via*: $\text{DH}(\text{MCl}_3\text{–Cl}) = \Delta H_f^\circ(\text{MCl}_3) + \Delta H_f^\circ(\text{Cl}) - \Delta H_f^\circ(\text{MCl}_4)$. ΔH_f° values were taken from ref. 26 ($\text{M} = \text{Ti}$) and ref. 27 ($\text{M} = \text{Si}$).

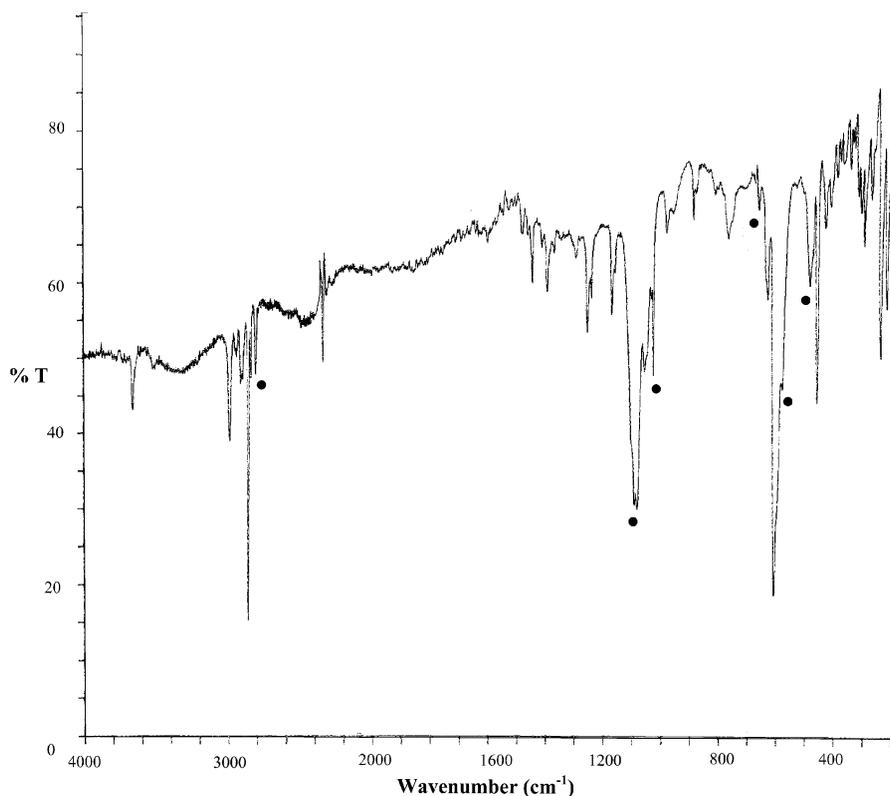


Fig. 4 Infrared spectrum (200–4000 cm^{-1}) of a low-temperature matrix (12 K) generated by condensing the products of the gas phase reagents Si_2Cl_6 (1 Torr), $\text{C}_2\text{H}_5\text{OH}$ (1 Torr) and Ar (200 Torr). The reagents were mixed at room temperature for 18 h prior to deposition. Bands of the species $\text{SiCl}_3\text{OC}_2\text{H}_5$, which is also formed when SiCl_4 reacts under similar conditions with CH_3OH , are identified by the symbol ●.

known that HSiCl_3 is much more reactive towards CH_3OH than is SiCl_4 .¹² However, there is no sign of the expected product of reaction, namely $\text{CH}_3\text{OSi}(\text{H})\text{Cl}_2$, nor is there any evidence from any of our reactions of a product containing an Si–H bond. These observations tend to disfavour the reaction pathway shown above.

An alternative is that one molecule of Si_2Cl_6 may react with two molecules of ROH ($\text{R} = \text{CH}_3$ or C_2H_5):



H_2 is not detectable by infrared spectroscopy and, in any case, it is non-condensable under our experimental conditions. In principle it could be seen mass-spectrometrically, but unfortunately our mass spectrometer is not configured to reliably detect ions at less than *ca.* 3 amu. It is noteworthy that reaction (3) is predicted to be more exothermic ($\Delta H^\circ = \text{ca. } -264 \text{ kJ mol}^{-1}$) than reaction (2) ($\Delta H^\circ = \text{ca. } -48 \text{ kJ mol}^{-1}$).[‡] Thus there is a considerable driving force in its favour. The presence of HCl in both mass and infrared spectra demonstrates that some further reactions also take place. The likelihood is that HCl is generated by further replacement of Cl atoms by OCH_3 groups which generates products such as $\text{SiCl}_2(\text{OCH}_3)_2$ and $\text{SiCl}(\text{OCH}_3)_3$. The ions $\text{SiCl}_2(\text{OCH}_3)^+$, $\text{SiCl}(\text{OCH}_3)_2^+$ and $\text{Si}(\text{OCH}_3)_3^+$ seen in the mass spectrum, provide strong evidence for this. In the infrared spectrum bands seen occur in the correct regions ($\nu(\text{C-H})$, $\delta(\text{CH}_3)$, $\nu(\text{C-O}$ or $\text{Si-O})$ and $\nu(\text{Si-Cl})$, see Table 3) of the spectrum to belong to one or more such molecules although precise assignments cannot be made.

[‡] These enthalpy change estimates are based on bond dissociation enthalpies listed in refs. 27 and 28.

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References

- 1 J. L. Speier and M. S. Tzou, *Organometallics*, 1993, **12**, 1981–1982.
- 2 W. C. Schumb and A. J. Stevens, *J. Am. Chem. Soc.*, 1947, **69**, 726.
- 3 W. C. Schumb and A. J. Holloway, *J. Am. Chem. Soc.*, 1941, **63**, 2753.
- 4 D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, 1946, **68**, 70–72.
- 5 W. Gerrard and A. H. Woodhead, *J. Chem. Soc.*, 1951, 519–522.
- 6 M. Binnewies and K. Jug, *Eur. J. Inorg. Chem.*, 2000, 1127–1138.
- 7 A. Kumar, T. Homann and K. Jug, *J. Phys. Chem. A*, 2002, **106**, 6802–6809.
- 8 R. Gooden, *Inorg. Chem.*, 1983, **22**, 2272–2275.
- 9 R. Gooden and J. W. Mitchell, *J. Electrochem. Soc.*, 1982, **129**, 1619–1622.
- 10 M. J. Almond and K. S. Wiltshire, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*, 2001, **97**, 3–60.
- 11 B. S. Ault, *J. Am. Chem. Soc.*, 1983, **105**, 5742–5746.
- 12 M. Brehm and B. S. Ault, *J. Mol. Struct.*, 2003, **649**, 95–103.
- 13 B. S. Ault and J. B. Everhart, *J. Phys. Chem.*, 1996, **100**, 15726–15730.
- 14 M. J. Almond and M. Hahne, *J. Chem. Soc., Dalton Trans.*, 1988, 2255–2259.
- 15 J. S. Ogden and R. S. Wyatt, *J. Chem. Soc., Dalton Trans.*, 1987, 859–865.
- 16 (a) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Ciolowski, J. V. Ortiz,

- A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A9*, Gaussian Inc., Pittsburgh, 1998.(b) J. B. Foresman and A. Frisch, *Exploring chemistry with Electronic Structure Methods: A Guide to Using Gaussian*, 1st edn., Gaussian Inc., USA, 1993.
- 17 A. Lee-Smith, *J. Chem. Phys.*, 1953, **21**, 1997–2004.
- 18 S. Woo Han and K. Kim, *J. Phys. Chem.*, 1996, **100**, 17124–17132.
- 19 J. Goubeau, F. Hänschke and A. Ruoff, *Z. Anorg. Allg. Chem.*, 1969, **366**, 113–115.
- 20 A. Ruoff, H. Bürger, S. Biedermann and J. Cichon, *Spectrochim. Acta*, 1974, **30A**, 1647–1651.
- 21 M. L. Delwaulle and F. Francois, *Compt. Rend.*, 1945, **220**, 817.
- 22 H. Gerding and Westrik, *Rec. Trav. Chim.*, 1942, **61**, 842.
- 23 A. J. Barnes, H. E. Hallam, J. D. R. Howells and G. F. Scrimshaw, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 738–741.
- 24 N. Goldberg, J. S. Ogden, M. J. Almond, R. Walsh, J. P. Cannady, R. Becerra and J. A. Lee, *Phys. Chem. Chem. Phys.*, 2003, **5**, 5371–5377.
- 25 N. Goldberg, PhD Thesis, University of Reading, 2003.
- 26 M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data*, 1985, **14**(Suppl. No. 1).
- 27 R. Becerra and R. Walsh, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, vol. 2, ch. 4, p. 153.
- 28 S. W. Benson, *Thermochemical Kinetics*, 2nd edn., Wiley, New York, 1976.