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The role of silylenes in the direct synthesis of methylchlorosilanes

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Abstract

From butadiene trapping experiments in a batch flow reactor, the silylene intermediates SiMeCl and $SiCl_2$ are shown to be formed during the Direct Synthesis. Two types of silylene intermediate are believed to be involved. Silylenoids are formed on the surface where they react with methyl chloride yielding methylchlorosilanes (SiMeCl gives Me_2SiCl_2, $SiCl_2$ gives $MeSiCl_3$) in accordance with the van den Berg mechanism. Free silylenes are released into the gas phase, where they may be trapped by butadiene, but are not directly involved in methylchlorosilane production. The addition of Me_3SiH to the methyl chloride promotes radical reactions; the major product is Me_3SiCl. Me_3SiCl is believed to result from an efficient chain sequence proceeding mainly on the surface involving $Me_3Si\cdot$ radicals which scavenge surface-bound chlorine.

Introduction

In the Direct Synthesis of methylchlorosilanes, methyl chloride gas is passed over solid silicon in the presence of a copper catalyst to produce dimethyldichlorosilane (DMDC) selectively; once formed, DMDC is then hydrolysed to form silicone polymers [1,2]. Although the Direct Synthesis was discovered fifty years ago, the mechanism for DMDC formation has not yet been firmly established. Whilst there is substantial evidence that the methylchlorosilane products are formed on the surface [2], little is known of the role of gas phase reactions in methylchlorosilane production.

Though the formation of gaseous methyl radicals during the Direct Synthesis has been demonstrated, they are not believed to participate in methylchlorosilane formation [1,3]. Proving the intermediacy of gaseous silyl radicals is more difficult as methyl chloride is a silyl radical transfer agent which will yield the appropriate chlorosilane [4]. It is however difficult to associate the high selectivity of the Direct Synthesis for DMDC with radical reactions [5]. Previous experiments have suggested the intermediacy of free silylenes, principally $:SiCl_2$ [2,6,7]. The possible

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involvement of silylenes in the Direct Synthesis is interesting because silylenes undergo very selective reactions [8] which in principle could explain the selectivity for DMDC, e.g. :SiMeCl + MeCl → Me_2SiCl_2, in addition to any surface reactions producing DMDC. The role of the copper catalyst is unknown, particularly as it is becoming apparent that the surface of the Si/Cu contact mass is silicon enriched [7,9,10]; that is, the surface composition is not that of the binary intermetallic compound Cu_3Si (the η-phase), previously believed to be responsible for the selective formation of DMDC [2]. However, one of the main roles played by copper is thought to be the weakening of silicon bonding in the Si/Cu contact mass and so silicon species formed on the surface may migrate into the gas phase [7,9,11].

Using a batch flow reactor coupled to a gas chromatograph/mass spectrometer (GC/MS) [12a,b], we have attempted to determine whether silylenes are formed during the Direct Synthesis of methylchlorosilanes.

Experimental

The contact mass used comprised technical grade silicon powder with a ca. 4% copper loading (donated by Dow Corning Ltd.). This mixture was placed into a batch flow reaction vessel, which was constructed so that the gas flow is directed over the metals, and activated in a static system under one atmosphere of methyl chloride gas at 648 K for ca. 3 hours and then at 606 K for a further 19 hours. The reaction vessel was evacuated, then filled with dry nitrogen, and inserted into a dry and deoxygenated GC/MS helium carried gas without exposure to the atmosphere. The reaction vessel containing the activated metals remained in the helium flow at a constant temperature (565 ± 1 K) whereupon trapping experiments were performed; the residence time of the pulse in the reactor was ca. 2.6 min. [12a]. Product analysis was performed using the GC/MS (HP5995C) equipped with a 50 m PONA capillary column (methylphenylsiloxane polymer). Gas phase samples of methyl chloride, admixtures of methyl chloride with buta-1,3-diene (Table 1), and methyl chloride with trimethylsilane were injected into the carrier gas from a vacuum line.

Results and discussion

Passing methyl chloride (MeCl) over the activated Si/Cu metals, in the absence of butadiene (C_4H_6), gave similar proportions of $MeHSiCl_2$, DMDC, and $MeSiCl_3$; a minor product appeared to be Me_2SiHCl.

Table 1

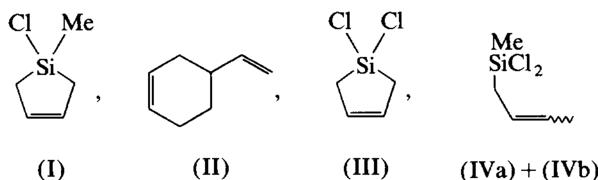
Composition of gas phase samples

Ratio MeCl : C_4H_6	Pressure (mmHg)	
	MeCl	C_4H_6
1:0	8.6	–
2:1	9.4	4.7
1:1	9.3	9.3
1:2	7.2	14.4
1:5	3.9	19.6
1:10	2.4	24.4

Buta-1,3-diene trapping experiments

To test for the formation of silylenes during the reaction of methyl chloride with the activated Si/Cu contact mass, various admixtures of MeCl : C_4H_6 (1 : 0–1 : 10) were passed over the activated contact mass; C_4H_6 has been shown to be an efficient trap for silylenes [13].

Passing a 2 : 1 MeCl : C_4H_6 mixture over the contact mass produced five new products in addition to $MeHSiCl_2$, DMDC, and $MeSiCl_3$, which increased with increasing C_4H_6 proportions. The new products were identified as:



(I) (II) (III) (IVa) + (IVb)

Compounds I, III, IVa, and IVb were all identified by comparison with the mass spectrum and the chromatographic retention time of the authentic compounds. With increasing proportions of C_4H_6, the new products increased at the expense of the methylchlorosilanes $MeHSiCl_2$, DMDC, and $MeSiCl_3$ (see Table 2). $MeHSiCl_2$ decreased rapidly with increasing butadiene proportions, and by 1 : 2 MeCl : C_4H_6 it had almost disappeared. DMDC and $MeSiCl_3$ were always produced even in the presence of a ten-fold excess of C_4H_6, but here DMDC was only just detectable. A minor additional product found when the C_4H_6 proportion was greater than two-fold, which is isomeric with II, was identified from its mass spectrum as octa-1,5-diene. Both II and octa-1,5-diene are the result of C_4H_6 dimerisation [14].

Passing the 1 : 10 MeCl : C_4H_6 mixture over the Si/Cu metals gave two new minor isomeric products which correspond to the general formula, Cl_3Si(butenyl). By analogy with IVa and IVb these isomers are judged to be *cis*- and *trans*-$Cl_3SiCH_2CH{=}CHCH_3$ (Va and Vb).

The formation of silacyclopent-3-enes I and III is good evidence for the presence of SiMeCl and $SiCl_2$ [13]. Their formation however does not indicate whether SiMeCl and $SiCl_2$ are free in the gas phase (silylenes) or bound to the metal surface (silylenoids). As the copper catalyst is reported to weaken silicon bonding in the contact mass [7,9,11] and the silylenes :SiMeCl and :$SiCl_2$ have been implicated in the Direct Synthesis [6,7], we believe that free silylenes are trapped by C_4H_6 to give I and III. Although silacyclopent-2-ene products, which are minor products of gas phase trapping of silylenes by C_4H_6 [13], were not detected, they are not expected as

Table 2

Product yields expressed as [product GC peak area/DMDC GC peak area]

MeCl : C_4H_6	$MeHSiCl_2$	DMDC	$MeSiCl_3$	I	II	III	IVa	IVb
1 : 0	1.12	1.0	1.11	–	–	–	–	–
2 : 1	0.95	1.0	0.85	0.14	0.14	0.33	0.79	0.40
1 : 1	0.85	1.0	0.93	0.44	1.31	1.26	1.47	1.30
1 : 2	–	1.0	1.32	0.48	3.05	2.57	2.09	1.69
1 : 5	–	1.0	2.41	0.55	12.56	9.24	4.05	3.41
1 : 10 [a]	–	1.0	9.01	1.18	92.35	634.20	9.77	7.09

[a] The yield of DMDC was very small.

the silacyclopent-3-ene adduct will be the major isomer by a factor of ca. 30 at 565 K [15].

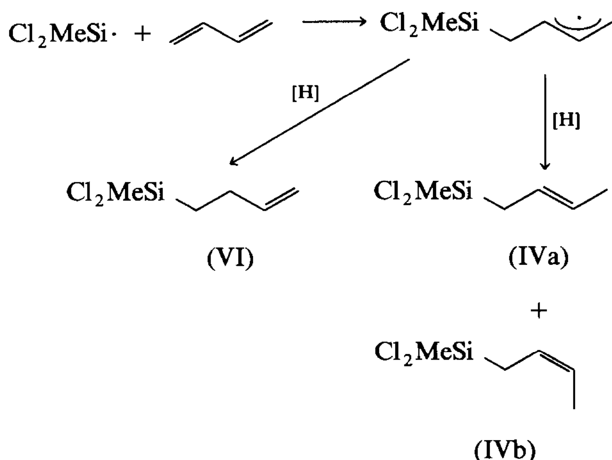
When :SiMeCl and :$SiCl_2$ were homogeneously generated in the gas phase in the presence of MeCl, insertion of these silylenes into the C–Cl and C–H bonds of MeCl did not occur readily [16]. At 565 K any homogeneous gas phase reaction between :SiMeCl or :$SiCl_2$ and MeCl should be negligible. This observation suggests that free :SiMeCl and :$SiCl_2$ are not important intermediates in the formation of methylchlorosilanes. Additional support for this suggestion arises from the continued production of methylchlorosilanes in the presence of C_4H_6. Methylchlorosilane (DMDC, $MeSiCl_3$) production was never completely inhibited by the addition of C_4H_6 to the MeCl pulse, though the proportion of methylchlorosilanes produced was progressively reduced when the C_4H_6 proportion in the MeCl : C_4H_6 admixture was increased. By 1 : 10 MeCl : C_4H_6, DMDC constituted a very minor product. Because C_4H_6 is a very efficient silylene trap [13], were :SiMeCl and :$SiCl_2$ important in methylchlorosilane formation then production should suffer dramatically when C_4H_6 is present. Methylchlorosilane production may have suffered in the presence of C_4H_6 because of, *inter alia*, competitive adsorption with MeCl on the metal surface, a problem which would increase with increasing C_4H_6 proportions. As the free silylene does not produce any major product by reaction with MeCl, then it must return to the surface to reconstitute an active site [17,18], in the presence of C_4H_6 its return will be inhibited and so methylchlorosilane formation would be affected. Furthermore, some C_4H_6 is expected to decompose on the metal surface serving to reduce the exposure of active surface sites to MeCl [19].

From the proportions of I and III produced (see Table 2) it can be seen that more :$SiCl_2$ is formed than :SiMeCl. Were free silylenes important in methylchlorosilane formation, it would be difficult to envisage how DMDC could be formed so selectively from :$SiCl_2$.

The formation of the acyclic *cis*- and *trans*-but-3-enylchlorosilanes, IVa, IVb, Va, and Vb, is interesting because if free silyl radicals participated in their formation, direct radical addition to C_4H_6 would be expected to produce three isomers in the ratio 2 : 1 : 1 (Scheme 1). Compound VI was shown not to be a product of the C_4H_6 trapping experiments after comparison of the mass spectra and the chromatographic retention times of IVa and IVb with an authentic sample of VI. The origins of IVa and IVb are not known, but they are possibly the result of surface reactions between C_4H_6 and $(MeSiCl_2)_{surf}$. Surface bound $(MeSiCl_2)_{surf}$ species are not novel and feature in several reaction mechanisms proposed to describe the Direct Synthesis [2]. The formation of small amounts of Va and Vb likewise suggest the formation of $(SiCl_3)_{surf}$, but in a smaller concentration than $(MeSiCl_2)_{surf}$ as Va and Vb constituted a very minor product in the presence of a large excess of C_4H_6. Acyclic butenylsilanes are not products of the gas phase homogeneous decomposition of silacyclopent-3-enes [15].

Trimethylsilane trapping experiments

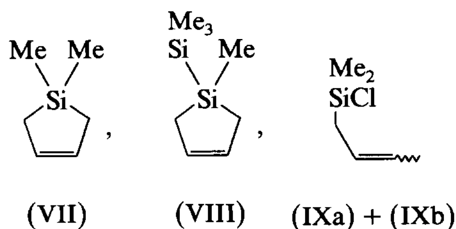
In order to confirm further the presence of silylenes, trimethylsilane (Me_3SiH), a silylene trap [20], was added to the MeCl pulse. A 1 : 1 MeCl : Me_3SiH mixture (partial pressure of each component was 6.5 mmHg) was passed over the activated Si/Cu metals used in the previous C_4H_6 experiments at 567 K. The products found were: methane, $SiMe_4$, a copious amount of Me_3SiCl, DMDC, $(Me_3Si)_2O$ (the



Scheme 1

hydrolysis product of Me_3SiCl), $Me_3SiCH_2SiMe_2Cl$, and $(ClMe_2Si)_2CH_2$. Passing Me_3SiH only over the Si/Cu metals at 565 K produced Me_3SiCl as the major product. Minor products comprised $Me_3SiCH_2SiMe_2Cl$, $Me_3SiCH_2SiMe_2H$, and $(Me_3Si)_2O$.

As none of the expected silylene trapping products ($:SiMeCl + Me_3SiH \rightarrow Me_3SiSiMeClH$; $:SiCl_2 + Me_3SiH \rightarrow Me_3SiSiHCl_2$) were observed, a ternary mixture of 1:1:1 $MeCl:C_4H_6:Me_3SiH$ (total pressure was 9.6 mmHg) was passed over the Si/Cu metals at 569 K. Again, Me_3SiCl was the major product, then $(Me_3Si)_2O$, and then DMDC (based on GC peak area); methane was also detected. Minor products found were I, II, $Me_3SiCH_2SiMe_2Cl$, $(ClMe_2Si)_2CH_2$, VII, VIII and IXa,b. Compounds VII, IXa, IXb, and $Me_3SiCH_2SiMe_2Cl$ were identified from their mass spectrum by comparison with authentic samples; VIII was identified on the basis of its mass spectrum only.



All the experiments in which Me_3SiH was present produced Me_3SiCl as the major product; at 567 K Me_3SiH is thermally stable to homogeneous thermolysis [21]. The formation of Me_3SiCl may be explained in terms of the following radical chain sequence (Scheme 2), which is similar to the reported radical sequence proposed to account for the formation of methane and Me_3SiCl when Me_3SiH and MeCl were thermolysed in a quartz vessel [22]. In that case, the reaction was initiated on the quartz surface and propagated in the gas phase.

$[\ ]_{surf} + MeCl \longrightarrow [Cl]_{surf} + Me\cdot$ (1)

$Me\cdot + Me_3SiH \longrightarrow Me_3Si\cdot + MeH$ (2)

$Me_3Si\cdot + MeCl \longrightarrow Me_3SiCl + Me\cdot$ (3)

$Me_3Si\cdot + [Cl]_{surf} \longrightarrow Me_3SiCl + [\ ]_{surf}$ (4)

$Me_3Si\cdot + Me\cdot \longrightarrow SiMe_4$ (5)

($[\ ]_{surf}$ represents an active surface site)

Scheme 2

Reaction 1, the initiation step (see also reaction 6 below), is supported by the reported formation of surface $(Si-Cl)_{surf}$ active sites [17], and the formation of methane; Me_3Si-H is a radical trap (reaction 2) owing to the weak Si–H bond [23]; MeCl is a silyl radical transfer agent (reaction 3) [4]. Reaction 4 is supported by the formation of a large amount of Me_3SiCl when Me_3SiH is passed over the Si/Cu metals (*vide infra*).

Reaction 6 is another radical initiation step which is also expected to be active in the presence of MeCl, and is proposed to account for the formation of Me_3SiCl when only Me_3SiH is passed over the Si/Cu metals.

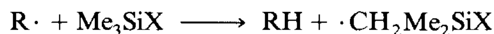
$Me_3SiH + [\ ]_{surf} \rightarrow Me_3Si\cdot + [H]_{surf}$ (6)

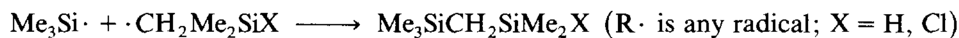
$Me_3Si\cdot + [Cl]_{surf} \rightarrow Me_3SiCl + [\ ]_{surf}$ (4)

The trapping of $:SiCl_2$ and :SiMeCl by Me_3SiH should produce the hydridodisilanes $Me_3SiSiHCl_2$ and $Me_3SiSiMeClH$, respectively; however in view of reaction 6 their absence is not indicative of the absence of free silylenes (at 567 K these hydridodisilanes would be thermally stable [24]).

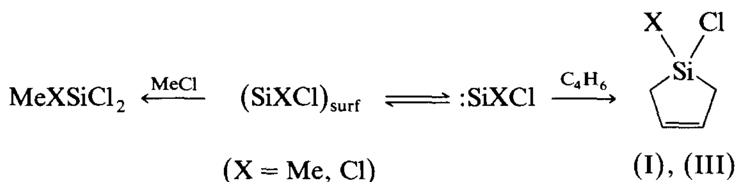
The absence of disilane products from experiments involving Me_3SiH implies that any radical chain sequence occurs at the metal surface. In all cases when Me_3SiH was present the major product was Me_3SiCl whose formation is reasonably explained by the reactions involving $Me_3Si\cdot$ radicals as indicated by reactions 4 and 6. In addition to the reactions forming Me_3SiCl, the reactions forming the disilylmethane products are also expected to be of a radical nature (*vide infra*) making the absence of any disilanes resulting from radical combination, in particular $Me_3SiSiMe_3$, more surprising.

The disilylmethane products were minor and so it is not possible to assign their origins, but several points may be noted. The formation of $Me_3SiCH_2SiMe_2X$ (X = H, Cl) suggests the common radical $Me_3SiCH_2\dot{S}iMe_2$. A well known route to this radical is via radical attack on $Me_3SiSiMe_3$ [25], but this route may be ruled out owing to the absence of any disilane products. On balance, the disilylmethane products are most likely the result of radical-like reactions occurring at the surface, for example:


$R\cdot + Me_3SiX \longrightarrow RH + \cdot CH_2Me_2SiX$


$Me_3Si\cdot + \cdot CH_2Me_2SiX \longrightarrow Me_3SiCH_2SiMe_2X$ ($R\cdot$ is any radical; X = H, Cl)

The formation of the silacyclopentenes I, VII, and VIII, as very minor products of the ternary mixture 1 : 1 : 1 $Me_3SiH : C_4H_6 : MeCl$, is indicative of the formation



Scheme 3

of :SiMeCl, $:SiMe_2$, and $:SiMe(SiMe_3)$, but these processes are very minor in comparison to the radical chain sequence producing Me_3SiCl. Again the small amounts of products other than Me_3SiCl prohibit any detailed discussion of their origins, but it is interesting to note the absence of $MeSiCl_3$ under conditions where DMDC, albeit as a minor component, was formed and to note the absence of III. $MeSiCl_3$ was also absent from the products of the 1 : 1 Me_3SiH : MeCl mixture even though DMDC was found.

A mechanism which describes the formation of methylchlorosilanes on the surface has been proposed by the van den Berg group [2,18]. The formation of :SiMeCl and $:SiCl_2$ may be accommodated by this mechanism as $(SiMeCl)_{surf}$ and $(SiCl_2)_{surf}$ intermediates participate in the formation of DMDC and $MeSiCl_3$ respectively.

A connection between I and DMDC, and III and $MeSiCl_3$ was also found in the pulse-flow experiments reported here (Scheme 3). The yield of I relative to DMDC (see Table 2) remained approximately constant between the proportions 1 : 1 and 1 : 5 MeCl : C_4H_6 indicating that an intermediate producing DMDC also produces I; by 1 : 10 MeCl : C_4H_6 the formation of I naturally increases over the formation of DMDC. The greater yield of III over I may be rationalised by the greater stability of $:SiCl_2$ [8]; orbital contraction induced by two electronegative chlorine atoms reduces reactivity [26].

When MeCl was passed over the Si/Cu metals in the presence of Me_3SiH, $MeSiCl_3$ was absent, though DMDC was a product. Similarly when MeCl was passed over the Si/Cu metals in the presence of both Me_3SiH and C_4H_6, $MeSiCl_3$ and III were missing. These observations may be explained by the scavenging of surface bound chlorine, i.e. $(SiCl_n)_{surf}$ ($n = 1–3$) [2]. If $(SiCl_2)_{surf}$ is an intermediate in the formation of $MeSiCl_3$, as suggested by the van den Berg mechanism, then as chlorine is scavenged by $Me_3Si\cdot$ radicals produced when Me_3SiH is present (reactions 4 and 6) the concentration of $(SiCl_2)_{surf}$ species is expected to fall and so the yield of $MeSiCl_3$ and III will decrease.

In summary, we believe that the silylenoids SiMeCl and $SiCl_2$ are bound to the surface of the contact mass and react with methyl chloride to produce DMDC and $MeSiCl_3$, respectively. These silylenoids may leave the surface to become free silylenes, probably as a result of the copper catalyst which weakens surface silicon bonding. The free silylenes, $:SiCl_2$ and :SiMeCl, do not react in the gas phase with methyl chloride to form methylchlorosilanes. When trimethylsilane is added to the methyl chloride pulse, trimethylchlorosilane is the major product which is believed to result from a radical chain sequence which involves trimethylsilyl and methyl radicals. The trimethylsilyl radicals abstract chlorine from methyl chloride and from the metal surface to give trimethylchlorosilane. The effect of abstracting the surface

bound chlorine is the reduction of the overall yield of methylchlorosilanes (other than trimethylchlorosilane which arises because of the trimethylsilyl radicals); chlorine-rich methylchlorosilanes, viz. $MeSiCl_3$, are most affected.

Acknowledgements

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