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THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES

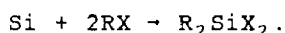
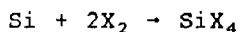
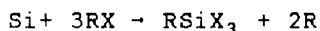
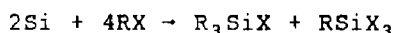
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INTRODUCTION

The Direct Synthesis (DS) is the industrial method by which methylchlorosilanes are prepared; principally dimethyldichlorosilane (DMDC) which is then hydrolysed to give polymeric siloxanes (silicones) [1,2]. The Synthesis itself involves the passage of methyl chloride (MeCl) gas over solid silicon, in a reaction catalysed by copper. Empirically, it is often summarised by the following simple equations:



The DS is remarkable because the selectivity for DMDC is typically 80-90% [3a], and it is further distinguished because the reaction between a gas (MeCl) and solid (Si) is catalysed by another solid (Cu).

The DS was first discovered independently by Rochow [4], Müller [5], and James [6,7] around 1940. Rochow found copper to be the best choice for catalyst; copper was known to be a catalyst for the reaction between silicon and hydrogen halides [8,9].

Since the discovery of the DS more than forty years ago, a great deal of effort has been levelled at trying to identify

the reaction mechanism and elucidating those conditions whereby DMDC is the only product. A great many industrial patents appear each year addressing this goal and describing the manipulation of the catalyst, for example $\text{CuCl}_n\text{-AlCl}_3$ ($n=1,2$) [10] which increases the rate of DMDC disproportionation to synthesise trimethylchlorosilane from DMDC and tetramethylsilane.

The early studies into the DS were plagued with problems owing to impurities in the silicon metal (and copper) capable of promoting the DS. Impurities can seriously affect the product composition, rate, and general properties of the contact mixture used in the DS. The reaction temperature required to form methylchlorosilanes decreases in the following order [11]:-

pure Si(99.9999%) > purified Si(99.8%) > technical Si (98%).

This problem was prevalent even up to the mid-1970's and was something which received the attention of Ward and coworkers [12] as recently as 1986. Not only did the purity of the materials render much of the early work unreliable, the experimental apparatus did not always ensure adequate heat conduction and this too affected results [3a].

The DS has been the subject of many reviews since the early 1960's, describing the enormous effort that the DS has rightly attracted. The first major review was by Zuckerman [13] in 1964 (this review contains 489 references), and was followed three years later by Voorhoeve's book [3], which is regarded as a landmark in DS literature describing his own extensive studies into the DS and of those up to the beginning of 1965. Bažant has written several reviews [7,14,15]. Gorbunov *et al.* [11] produced a review in 1974 reviewing work up to 1972, and Turetskaya *et al.* [16] reviewed the mechanisms proposed for the DS up to 1975. The reader should not forget the work of Trambouze [17] which although flawed by some of the above points, was the first extensive study and gave a flavour of things to come.

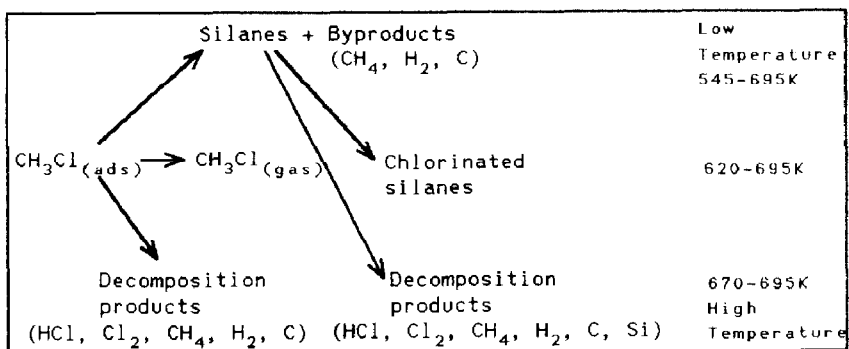
THE SYNTHESIS AND CONTACT MIXTURE

Methyl chloride is reacted with solid silicon in the presence of a copper catalyst between 553 and 623K [3a] to give DMDC as the major product; other products formed in smaller amounts are $\text{Me}_{4-n}\text{SiCl}_n$ ($n=1,3$), MeHSiCl_2 and Me_2SiHCl , and these constitute the low-boiling fraction. The high-boiling fraction contains chlorinated disilanes, chloroalkylsilanes and disilylmethanes (and some siloxanes) [18]. Non-silicon containing products formed are mainly hydrocarbons, principally methane. The hydrocarbon by-products of the industrial DS have been shown to comprise twenty-four hydrocarbons ranging from methane to diethylbenzene [19].

Temperature is crucial in determining the *rate* of reaction, but within the range 553 to 623K, the *product* composition does not vary greatly [3a,12,20]. Methyl chloride does not react readily with pure silicon, as demonstrated by Falconer and Frank [21], and only after a lengthy induction period (to be discussed) does chlorosilane production begin. On Si(100) the induction period was 31h. at 670K then 9h. at 695K, with a methyl chloride pressure of 84 kPa. The principal products during steady-state reaction between Si(100) and methyl chloride were HSiCl_3 and MeHSiCl_2 (545-620K); product distributions found at 545K were 74% and 18% respectively, with DMDC found as a minor product (4% at 545K). Owing to the lengthy induction period, the reaction between pure silicon and methyl chloride is considered erratic and irreproducible [3a,21]; some workers conducted their experiments during the induction period [4,21]. Trichloromethylsilane is the only methylchlorosilane formed during the induction period with Si(100), however this gives way to HSiCl_3 and MeHSiCl_2 during steady-state conditions, where MeSiCl_3 falls to 1.2% at 545K. The reaction sequence on silicon may be summarised by the following scheme:

SCHEME 1

Reaction Pathway for Methyl Chloride on Si(100)



[Source: ref. 21]

Ward *et al.* [12] have shown, when using Sn/Cu and Zn/Cu catalysts, that a 20K rise (573-593K) in temperature increases the reaction rate by a factor of approximately 2.4. Like temperature, pressure does not affect the product distribution [3b,12,20] but owing to the dependence of reaction rate on the partial pressure of methyl chloride (see later) optimum pressures between 4 and 7 atmospheres have been proposed [7,22]. One thing quickly becomes clear when surveying the DS literature: the composition of the contact mass is more important in affecting product distribution and rates than the general experimental parameters ($T=573\pm 50K$) [3a,20].

Voorhoeve [3c] described the contact mass as the 'mixture of silicon, catalyst and other substances prepared in a mechanical, physical or chemical process'. The contact mass may be prepared in a variety of ways, simply as is done industrially by the mixing of silicon and copper powders [3d,4,23] (with typically [3a] 5-10% wt. Cu); other methods include introducing copper in the form of copper(I) chloride [24] or copper oxide [25], or as an alloy (see later) [3,12,26-28]. The mode of copper incorporation into the contact mass has a great effect on the DS, thus when the two powders silicon and copper are mixed, methylchlorosilane production does not start immediately. In fact, no methylchlorosilanes are observed for several hours. Instead

methane, hydrogen and carbon (deposited on the surface) are produced [3d,4,17]; this is the induction period (discussed below). It is most pronounced in the reaction of methyl chloride with silicon [21] in the absence of copper.

THE Cu_3Si (η) PHASE

The catalytic activity of copper lies to a very great extent in its ability to form the binary intermetallic compound Cu_3Si (η -phase). The η -phase is that phase formed by the largest dissolution of copper in silicon (silicon content $> 12\%$ -wt. Si) [3a]; where silicon and copper are in thermodynamic equilibrium, the result is free silicon and η -phase. Trambouze [17] first discovered its significance but it was not generally accepted to be the key to the catalytic process, for example Krylov and coworkers [29] discovered Cu_3Si in their contact mass (prepared from fusing 24.7%-wt. Cu with Si in an induction furnace) but attributed the catalytic activity directly to free copper, which was produced by the breakdown of Cu_3Si to give a uniform and highly dispersed reactive copper catalyst, a view later echoed by Turetskaya and coworkers [16,30] and Müller [31]. Substantial evidence now confirms Cu_3Si (η -phase) as being of great importance; Voorhoeve and coworkers [3d,24,32] discovered that Cu_3Si was formed in all contact mixtures with the formation of methylchlorosilanes. Falconer and coworkers confirmed that the Cu_3Si phase provides an active surface for DMDC formation, the stoichiometry of which alters with reaction [27]; a clean Cu_3Si surface is not catalytically active until the silicon is bound to chlorine (see later). Areal reaction rates determined by Falconer agree with those found by Voorhoeve *et al.* [32] who used fluidised mixtures of silicon and copper, yielding 5×10^{14} Si atoms. $\text{cm}^{-2}.\text{s}^{-1}$ and 3×10^{14} Si atoms. $\text{cm}^{-2}.\text{s}^{-1}$ at 540K respectively. Furthermore it became apparent that the long induction period seen with powdered mixtures of silicon and copper is required to form the η -phase [24,27,33]. In addition, it is known that in the equivalent of the DS for tin and germanium, the intermetallic compounds Cu_3Sn and Cu_3Ge are instrumental [3d].

The DS is itself one of the best methods for forming Cu_3Si from powdered silicon and copper mixtures. Mixing the two metals in an inert atmosphere requires a great deal of heat before the alloy is formed. Trambouze [17] and others [3a] showed for a mixture of silicon and copper powders, it is necessary to heat the mixtures at 1073 to 1373K in nitrogen (or hydrogen when CuO is used) before the powders sinter and form the Cu_3Si alloy.

The temperature during the DS does not generally exceed 623K (excessive heating causes deactivation of the catalyst, e.g. heating at 923K for several hours [3e]); that temperatures in excess of 1073K are required for the formation of Cu_3Si suggests that the formation of Cu_3Si during the induction period is a chemical process. It should however be noted that the η -phase is not the only catalytic phase of binary copper-silicon mixtures. Using a fluidised-bed reactor, Voorhoeve and coworkers [24a] showed that the ϵ -phase ($\text{Cu}_{15}\text{Si}_4$) has some catalytic activity though soon suffers a dramatic loss of selectivity, presumed to be due to the large amount of copper produced after silicon is removed by reaction with methyl chloride. This latter copper silicide and other silicides, Cu_xSi_y , have been shown to be unstable with respect to decomposition to copper [24b]. As Voorhoeve notes [3d], when the reactive phase is referred to as the ' η -phase', this generally means all three [34]: η , η' , and η'' , because they are difficult to distinguish by X-ray diffraction.

THE INDUCTION PERIOD

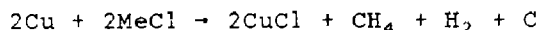
Regarding the induction period, the longest is found with straightforward mixtures of silicon and copper powders [33], and silicon alone [21], whilst the shortest was found with the Cu_3Si alloy [27,28]. The induction period is the period when the active surface for methylchlorosilane production is formed. If the Cu_3Si phase is not already present it is produced during this period and subsequently the active surface is formed [21,26-28].

TABLE 1
Induction Times

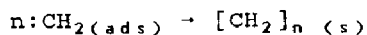
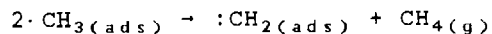
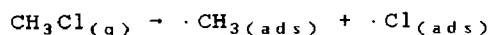
INDUCTION TIMES		
SURFACE	TEMP./K	INDUCTION TIME (MINS.)
Cu ₃ Si	520	1000
	540	60
	570	40
	595	<5
Cu ₃ Si-Zn	545-615	<5
Si(100)	678, 695	>2000

[Source: ref. 27]

During the induction period, initially no silanes are found [3b,21,33]; methane, hydrogen and carbon (deposited on surface) being formed instead. These products are believed to be the result of the cracking of methyl chloride on the copper [3d,14,22,25,33-36], empirically:



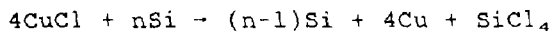
Bažant and coworkers believe that the non-volatile products resulting from decomposition of methyl radicals (*i.e.* $\cdot\text{CH}_3 \rightarrow \text{C} + 1\frac{1}{2} \text{H}_2$), may consist of polymethylenes formed on the surface of the catalyst [7,14]:



Anderson and McConkey [36] using evaporated films determined that adsorption of methyl chloride on copper resulted in C-Cl bond rupture before any C-H bond rupture, giving methane and hydrogen. In addition they found that no chlorine was returned to the gas phase, possibly suggesting the formation of copper chloride. The formation of copper(I) chloride is believed to be instrumental in the formation of Cu₃Si from free copper [25] and silicon; it is also believed to act as an initiator in the formation of surface

silicon-chlorine active sites (see later). The view that cracking of methyl chloride on free copper is a primary process is shared by Voorhoeve and Vlugter [3a,33]. These authors inhibited the cracking of methyl chloride on free copper, formed as a result of reaction of methyl chloride with η -phase, by the addition of 1 vol.% hydrogen sulphide in the methyl chloride flow (for 1h. at 608K), which gave a sharp rate increase without affecting selectivity. Here the copper(I) sulphide formed could easily be removed to expose unreacted η -phase, thereby forming methylchlorosilanes rather than copper(I) chloride.

Copper(I) chloride is generally used in practical studies for DS contact mass [3a,11,13,14,16,33,38]. It is noted that for this contact mixture there is only a short induction period during which time products are typically rich in chlorine, often represented [3a,33,39]:



Silicon particles coated in Cu_3Si were reported when copper chloride and silicon were introduced as the contact mixture [3a,24,33], supporting an earlier suggestion that copper chloride is involved in the formation of Cu_3Si [25]. Copper(I) chloride can exist as Cu_3Cl_3 which was suggested may be more reactive as the trimer [16]; $\text{Cu}_3\text{Cl}_3(\text{g}) \rightleftharpoons 3\text{CuCl}(\text{g})$ [$K(1000\text{K})=1.15 \times 10^{-13}$], low temperatures favour the trimer [40-42].

There have however been problems associated with the idea that methyl chloride cracks on free copper to give copper chloride and subsequently, in the presence of silicon, yield Cu_3Si [3a,39]. It was Rochow and Hurd [23] who noted the rapid and exothermic reduction of copper chloride by elemental silicon at 538K, which is a problem insofar as the DS is known to operate at temperatures below 538K. The situation with respect to this criticism is not clear as much of the work on which it was based [3d,39], was performed before the importance of promoting impurities was realised. The diffusive properties of copper in silicon to form the Cu_3Si phase have been

investigated (see later), and it is now generally believed that as a result of the rapid diffusion of copper, the η -phase is formed [37,43,53].

The formation of copper(I) chloride during the induction period, a process first discovered by Rochow and Hurd [23], is desirable in light of a recent discovery that methylchlorosilane formation occurs at surface SiO_2 defects (to be discussed) [43]. Formation of copper(I) chloride 'satellites' centred around SiO_2 surface defects after gas phase copper(I) chloride transport have been reported, thereby placing copper catalyst at the sites of methylchlorosilane formation [43,69].

An insight into the reason for a Si/CuCl contact mass having a small induction period before selectively generating DMDC comes from the work of Falconer and coworkers [21,28] (see also Ring and coworkers [44]). Using Auger Electron Spectroscopy (AES) to monitor the composition of the surface of silicon [21] and Cu_3Si [28] in a batch reactor before and after reaction with an atmosphere of methyl chloride, they were able to characterise the surface of the solid phase. They found in the case of silicon without any added copper: silicon, chlorine, oxygen and carbon on the surface; for Cu_3Si : silicon, copper, chlorine, carbon and oxygen. The silicon LVV (*L shell-valence-valence*) Auger transition gave evidence for Si-Cl and Si-C bonds (on Si(100) the carbon is graphitic whereas on Cu_3Si it is present as the carbide; signals were seen from Si-Cu bonds in the Cu_3Si alloy). This led to the conclusion that active sites are those where silicon is bound to chlorine, *i.e.* Si-Cl; the process occurring during the induction period. The idea of surface silicon bound to chlorine is not a new one and features in many reaction schemes [3d,23,25,35,37,45-52].

Since methyl chloride is known to break down on copper to form copper chloride [3d,14,22-25,33,35,36] and copper (in the presence of excess silicon) diffuses rapidly to give Cu_3Si [37,43,53], it can therefore be envisaged that the remaining process during induction is chlorine transfer to silicon forming active Si-Cl sites [21,28]. If the copper is introduced as copper(I) chloride, the smaller induction periods

would be expected to consist of the formation of Cu_3Si and Si-Cl active sites. The longer induction period experienced with copper and silicon powders is attributable to the initial formation of copper(I) chloride [3d,24,33]. The copper(I) chloride must be required only to form the η -phase and Si-Cl sites and not directly to catalyse the formation of methylchlorosilanes because surface analysis using AES [28] (84kPa over Cu_3Si and Cu_3Si -0.4 at% Zn between 520 and 620K) and XPS/ESCA [54,55] (between 573 and 673K) did not report any Cu-Cl bonds. When using only the Cu_3Si phase [21] the short induction period involves the formation of Si-Cl active sites.

The foregoing suggests that the formation of the η -phase (when not already present) is a chemical event, and so temperatures of the order 1073-1373K are not necessary; copper(I) chloride is observed during the DS [3d,24a,25,33] and is known to be a chlorinating agent of silicon. Hence, after chlorine transfer to silicon to form active sites, free copper is then able to diffuse into the silicon to form the Cu_3Si phase. As will be discussed, the rapid diffusion of copper in silicon [37,43,53] appears to favour such a process.

Evidence in favour of the formation of Si-Cl active sites is the use of chlorine and hydrogen chloride gases (chlorinating agents) which can affect the induction period, shortening it and altering the product composition when added to the methyl chloride flow [3a,14-16].

PHYSICAL PROPERTIES

As Hansen [34] has shown, the copper-silicon system is complex and consists of many different phases which show a marked dependency on temperature and proportions of silicon and copper present. Using a Si/Cu alloy consisting of two phases, silicon and intermetallic Cu_3Si with impurities, Lobusevich *et al.* showed by microstructural analysis that the impurities were not randomly distributed throughout the silicon or Cu_3Si phase [56]; they discovered that silicon does not exist as a monophase, in fact macro impurities form structural components. These results indicate that Cu_3Si is free from impurities: iron

is present as FeSi_2 (ζ -phase) and is found distributed at the boundaries of the silicon grains, and calcium is likewise present as CaSi_2 and located at a boundary with FeSi_2 . Similar results are seen with aluminium (present as a eutectic mixture: 15% Si, 40% Cu and 35% Al), where it is found between silicon grains, Cu_3Si , and FeSi_2 . Here it was claimed that the addition of iron stabilises the catalytic activity of Si/Cu alloys by making them less sensitive to impurities as it has the effect of concentrating impurities at its boundaries, and so keeping the Cu_3Si free. Later work refined this idea concluding that the multi-component phase formed with iron, *i.e.* Fe-Si-Ti-(Mn)-(V)-(P) removes impurities Ti, Mn, V and P which exert an unfavourable influence on the DS; this phase does not react with methyl chloride [57].

Work was later undertaken studying changes during the DS of the impurities: V, Mn, Mg, S, Se, Te, P and Bi [57]. Analysing concentration curves of radiation intensities for commercial silicon two types of environment were identified, metallic and non-metallic. Metallic iron was found as FeSi_2 (ζ -phase: 49% Fe + 52.5% Si). A complex metallic inclusion containing the following was also observed: Fe(28%), Ti(30%), Si(28%), Mn(0.5-2.5%), V(1-3%) and P(0.5-1.5%). Non-metallic inclusions included complex oxides (quartzites), Fe-Al-Ca-Mn-O and Si-Al-Ca-O, containing: Fe(45%), Si(25%), Ca(6%), Mn(0.5%), Al(15%) and oxygen. Non-metallic inclusions had a nonhomogeneous surface making analysis difficult. In low concentrations Mg, Se, Nb, Te, and Bi were found in a silicon matrix or at inclusion boundaries. Alloying commercial silicon with 2% Ca produced CaSi_2 . Additional impurities in commercial silicon are FeSi_2 , an inclusion formulated as Ca-Al ($\leq 30\%$ Si) and a multicomponent phase, Fe-Si-Ti-Mn-V-P (Mn, V, and P were not always present in this phase). Reaction of the latter contact mixture (alloyed with either 2% Ca or Al) with methyl chloride at 673K gave chlorinated inclusions containing CaSi_2 , Fe-Al and Ca-Al phases. No chlorine was found on the surface of the above multiphase component. The FeSi_2 was found not to react with methyl chloride.

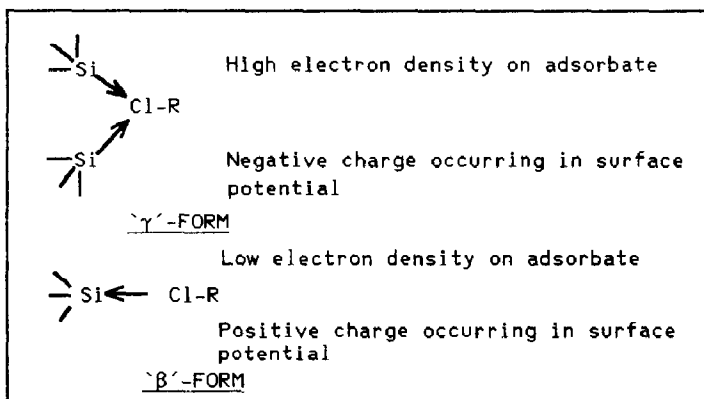
To understand the DS it became necessary to establish

whether the DS is a purely heterogeneous or heterogeneous-homogeneous process, e.g. with species formed on the surface desorbing into the gas phase where reaction leads to products. Hurd and Rochow [23] thought of the process in this fashion, with gas phase entities like methylcopper and methyl radicals. The position is not clear, but many [3d,14,15,17,22] believe that methylchlorosilane production is a heterogeneous event with reaction occurring on the surface. Calorimetric experiments [11,58-60] indicate that the exothermic reaction steps for reaction of silicon with hydrogen chloride (to form HSiCl_3) occur on the surface of the contact mass [58]. The temperature of a silicon layer coating the reaction vessel and the centre of the reaction vessel were recorded and the difference between these two temperatures was monitored with time [58-60]. For low reaction periods (to ensure constant silicon reactivity) this difference was zero, suggesting that exothermic reaction steps take place on the silicon surface. It is important to note that in these studies [58,60] copper was absent. In addition to calorimetric studies, experiments involving the use of radical initiators and promoters also agree with the conclusion that methylchlorosilane formation is a heterogeneous process [3d,14,15,61,62]. The majority of workers believe that the DS is indeed heterogeneous, however some Russian workers do not consider all the reactions steps resulting in the formation of methylchlorosilanes take place on the solid surface (see later).

Voorhoeve [3f] noted that neither temperature nor pressure had any marked affect on the selectivity of the DS and claimed that any selectivity was a direct function of the solid phase (as will be seen in the mechanistic section later). The view that the DS was purely heterogeneous and that the selectivity was the result of a particular solid phase (*i.e.* the Cu_3Si phase), led to a large concerted effort to investigate the general properties of the contact mass. Work concentrated particularly on the adsorption and diffusion properties of the contact mass.

Surface potentials resulting from adsorption of RCl and HCl on silicon have demonstrated that the chlorine can attach

itself to silicon in one of two forms, β and γ [47]. Formation of these adsorption complexes is believed to enhance the reactivity of silicon, making it a suitable substrate for the DS [47,63]. In the γ form, silicon acts as an electron donor using free sp valences, and chlorine acts as an acceptor with its vacant $3d$ orbitals. In the β form it is chlorine which acts as electron donor, donating its $3p$ electrons and silicon as acceptor, using vacant $3d$ orbitals. Diagrammatically, these forms may be represented as:



In similar work, the effect of copper was investigated using the contact potential difference method [63]. After exposure of pure silicon to methyl chloride no β -adsorbate (in this work the two forms β - and γ - are referred to as type I and II respectively) was found; it appears only at 376K. The β form was present however at 298K on a Si/Cu alloy (containing 2.4% copper), from which it did not desorb at 298 nor 368K in an evacuated chamber, suggesting that the β -adsorbate is tightly bound. The γ -adsorbate resulting from exposure of pure silicon to HCl was more tightly bound than the β -form, increasing in amount with increasing temperature. A Si/Cu alloy (2.4% Cu) showed no γ -adsorbate at 393K, only increasing in amount at low temperatures (298-358K) and was easily desorbed during evacuation of the system at 298 and 358K. Increasing the proportion of copper in the alloy to 8.63%, saw no γ -adsorbate formed even at 298K. The addition of copper made the β -adsorbate more firmly bound than on pure silicon,

but the converse is the case with the γ -adsorbate. Thus it would appear that copper affects the adsorption of methyl chloride and hydrogen chloride on silicon such that in the presence of copper, adsorption is reversible at lower temperatures compared to adsorption on pure silicon. For example, adsorption of hydrogen chloride (β - and γ - adsorbates) shows total reversibility at 393K on a Si/Cu alloy (2.4% Cu), compared with near total reversibility on pure silicon at 501K; methyl chloride shows appreciable reversibility for both forms of adsorbate on a Si/Cu (2.4%) alloy at 501K. The similarity found between the contact potential for adsorption of methyl chloride and HCl on both Si/Cu alloys and pure silicon, suggests that adsorption takes place on silicon. Later it was shown that the ΔH_{ads} for hydrogen chloride adsorption is in favour of adsorption through chlorine [64]. Estimates for the enthalpy of adsorption for methyl chloride have been reported as: $-88.2 \text{ kJ.mol}^{-1}$ on technical silicon, $-19.7 \text{ kJ.mol}^{-1}$ on pure silicon and calculated as $-97.6 \text{ kJ.mol}^{-1}$ and $-88.2 \text{ kJ.mol}^{-1}$ on a silicon-copper contact mass [65]. Kunzru and coworkers [66] modelled the formation of methylchlorosilanes on a silicon-copper contact mixture and determined the equilibrium constant for adsorption of methyl chloride to be:

$$K_A = 1.1 \times 10^{-4} \exp \left\{ \frac{2373.7}{T} \right\} (\text{atm}^{-1})$$

From X-ray crystallographic studies [3d] of η -phase containing contact mixtures as a function of silicon conversion, it was shown that after ca. 30% silicon conversion the composition of the contact mixture was that of the γ -phase, that is, it consisted of the ϵ -phase ($\text{Cu}_{15}\text{Si}_4$) and free copper [3d,24b]. This discovery was interpreted as proof of rapid diffusion in the solid, which was just not fast enough to establish a thermodynamic equilibrium. Using a eutectic alloy consisting of 30% atm-Si and η -phase, the diffusing element was believed to be silicon. Silicon diffused from the free state into the Cu_3Si phase to reconstitute it after silicon had been removed by reaction with methyl chloride. In this eutectic mixture 78% of silicon is linked to the copper and 22% is free.

It was noted that when the selectivity was monitored with %Si conversion, the selectivity for DMDC was high up to ca. 22%Si conversion, whereupon DMDC began to fall and highly chlorinated products (e.g. trichloromethylsilane) began to rise owing to the build up of free copper.

Gupta and Sharma found that after ca. 20% silicon conversion, silicon segregates to the surface of a Si/Cu alloy where its concentration increases from 2.6 at% in the original contact mass to 16.7 at% [54]. The authors interpret this increase as rapid non-rate limiting silicon diffusion. Falconer and Frank using alloys of composition, $\text{Cu}_{0.95}\text{Si}_{0.05}$ and Cu_3Si , had earlier found that silicon segregates to the surface at 570K, increasing for Cu_3Si above 670K to give alloyed and non-alloyed silicon [67]. These latter results were assigned to surface tension differences between silicon and copper which in addition with the Burton and Machlin Rule predict silicon segregation. Surface silicon enrichment has also been reported by M^oLeod [68] both in an oxidised sample of Cu_3Si (studied by XPS between 296 and 773K) and an unoxidised Cu_3Si sample after heating in a vacuum.

Surface silicon concentration for reacting Cu_3Si has been reported by Banholzer *et al.* [69], who found that the Cu/Si ratio varies between <0.5 to 2 (with 20-50% accuracy). This result is important because it indicates that in the reacting regions of the surface, Cu_3Si is not present therefore casting doubt as to whether Cu_3Si is the active phase in the DS. Bulk copper however is present as the n-phase, it is only the surface which is silicon enriched [69].

Falconer has developed a model for the diffusion of silicon in the Cu_3Si phase [27]. In his work, unlike that of Voorhoeve [3d] (above), the silicon converted into silanes could not be replenished from free silicon present in the contact mass. Falconer found that after induction of the catalyst, reaction rates on Cu_3Si decreased with time and attributed this to silicon diffusion. To confirm that this decrease was in fact due to silicon diffusion and not equilibrium effects, he produced the following model which fitted experimental data and gave D (silicon diffusivity) with

a $\pm 5\%$ precision:

$$C_g = \frac{0.25AC^2D}{V_r k} \left\{ \exp\left(\frac{k^2 t}{C^2 D}\right) \left[1 - \operatorname{erf}\left(\frac{kt^{1/2}}{CD^{1/2}}\right) \right] + \frac{2kt^{1/2}}{CD^{1/2}\sqrt{\pi}} - 1 \right\}$$

{A = reacting Cu_3Si surface area; V_r = reactor volume; t = reaction time; D = silicon diffusivity; C = atomic density; C_g = gas phase product density; k = rate constant; erf is the error function and is defined by: $\operatorname{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-y^2} dy$. }

From this modelling an activation energy of $252 \pm 42 \text{ kJ.mol}^{-1}$ for silicon diffusion is reported.

Ward and Carroll [53] studied diffusion of copper and silicon to form the Cu_3Si phase. Electroplating copper onto silicon wafers (containing ≈ 20 ppb of boron) produced a phase containing 75.2% Cu and 24.8% Si (molar amounts). For the temperature range 523 to 623K, the activation energy for diffusion of copper in silicon was found to be 97.4 kJ.mol^{-1} . Veer *et al.* [37] studied the formation of the Cu_3Si phase from copper and silicon, determining the activation energy to be $\leq 78.1 \text{ kJ.mol}^{-1}$. Ward and Carroll [53] recalculated this activation energy from results listed by Veer [37] and report a different, corrected value for copper diffusion as $106.3 \text{ kJ.mol}^{-1}$. The apparent ease of copper diffusion in silicon relative to silicon diffusion in copper prompted the suggestion that if free elemental silicon is present in the contact mass, copper will diffuse to give the Cu_3Si phase [43].

It would therefore appear that when free silicon is present in a contact mass, copper diffuses to form Cu_3Si [27]. However, once the η -phase is formed, silicon is required to diffuse to the surface and replace the silicon removed by reaction; neither silicon nor copper diffusion is considered to be rate determining [70].

Falconer's was not the first modelling for diffusion of silicon within a silicon-copper contact mixture, although it was for a purely Cu_3Si contact mixture. Kunzru and coworkers [66] modelled the copper catalysed DS between 573 and 623K; their modelling resulted in the following equation for silicon

diffusivity:

rate of input of Si
into single η -phase
crystallite by surface
diffusion $= 2\pi D_{Si} r_{\eta} (0.037 - C_{Si\eta})$, gmol.s^{-1}

{ D_{Si} = surface diffusion coefficient, $\text{cm}^2.\text{s}^{-1}$; r_{η} = radius of phase crystallite, cm; $C_{Si\eta}$ = concentration of Si in the η phase, gmol.cm^{-3} .}

This model contains two incorrect assumptions: (1) that added copper reacts instantaneously with silicon to form the Cu_3Si phase, although it is known that the formation of Cu_3Si comes only after a lengthy induction period [3a]; (2) that the Cu_3Si phase becomes the ϵ -phase through reaction (and that below 10.4-wt% Si, no Cu_3Si is present) and the ϵ -phase has no reactivity, although it has been demonstrated to possess limited reactivity [3a,24,70].

Agarwala and Falconer used a zinc doped η -phase ($\text{Cu}_3\text{Si} + 1.2\text{-at\% Zn}$) contact mass and found that as a result of the addition of zinc, selectivity for DMDC is very high and the reaction rate remains unaffected [26]. They concluded that if zinc is present in a small amount silicon diffusion is no longer limiting. Zinc has also featured recently in the work of Ward and coworkers [12] who note that both zinc and tin are potent promoters of DMDC selectivity and when present together in suitable amounts, they show a synergistic effect; between 548 and 648K the selectivity for DMDC was reproducibly $\approx 90\%$. There have been several suggestions concerning the favourable effect of zinc. Agarwala and Falconer concluded in their study that zinc alters the morphology of the Cu_3Si phase such that diffusion does not limit the reaction rate [26]. The $\text{Cu}_3\text{Si-Zn}$ surface of a Cu_3Si -contact mixture containing 0.4-at% Zn, was found (using AES surface analysis) after reaction with methyl chloride, to contain up to 85% graphitic carbon, whereas the carbon present on a Cu_3Si -contact mixture was in the form of the carbide [28]. This difference prompted Falconer to suggest that zinc may be responsible for converting the carbide to graphite, thereby freeing some active sites. Zinc has also

been proposed to scavenge oxygen but this turned out not to be the case [68]; using XPS to study the exposure of sputtered Cu_3Si to 1 torr of oxygen, one-third of the silicon became SiO_2 but zinc was not oxidised. More recently it has been proposed that the addition of zinc to the contact mass serves to maintain a constant surface reaction environment, thus enabling a persistent selectivity for DMDC formation; because copper and silicon diffusion rates are not rate determining [69,70]. Tin, another common promoter, assists reaction because as tin diffuses in the solid, the grain boundaries are embrittled resulting in an increase in the reaction surface [70].

SURFACE OXIDATION

The Cu_3Si phase was shown to be very susceptible to oxidation, a black oxide coat is formed after less than twenty-four hours exposure to air at room temperature, whereas $\text{Cu}_{0.95}\text{Si}_{0.05}$ shows almost no corrosion even after several months exposure [67a]; in a different study, a two week exposure to air produced a SiO_2 layer 3600Å deep whilst copper remained unoxidised [67b]. Surface oxygen was concluded to affect the overall rates for silane formation by blocking active sites [71]. In the presence of oxygen, methyl chloride breaks down more rapidly, but the rate of formation of DMDC remains constant; the overall effect of surface oxygen is manifested in a significant decrease in DMDC selectivity. McLeod *et al.* found similar results; the Cu_3Si phase is more reactive towards oxygen than $\text{Cu}_{15}\text{Si}_4$ (ϵ) and Cu_5Si phases [68]. Using XPS binding and peak intensities CuO and SiO_2 were observed. Formation of SiO_2 served to block active sites but once removed, methyl chloride adsorbs as normal.

De Cooker *et al.* found that the addition of 1000ppm of oxygen to the methyl chloride flow had no effect on the product selectivity, but sharply reduced the rate of reaction (by 65% of the original value found in the absence of oxygen) [72]. Greater concentrations of oxygen affected the selectivity, and by 5000ppm selectivity had decreased by 10%. When oxygen addition was stopped the original selectivity was restored but

not the original reaction rate. For temperatures between 588 and 613K and low methyl chloride conversions (3.3 to 15.4%) the above authors described the effect of oxygen on the DS by a Langmuir type adsorption analysis for both oxygen and methyl chloride. It was concluded that the effect of oxygen may best be described by a dual site adsorption mechanism forming a very stable surface oxygen species; $K(O_2) = 421 \text{ atm}^{-1}$ for $O_{2(gas)} \rightleftharpoons O_{2(ads)}$.

It has been shown that reaction between silicon and methyl chloride occurs at surface SiO_2 defects (in agreement with the observation that DMDC is formed at a constant number of surface sites [26,71]) and cleaning the silicon surface with hydrofluoric acid increases the density of surface defects [43].

ROLE OF COPPER AS CATALYST

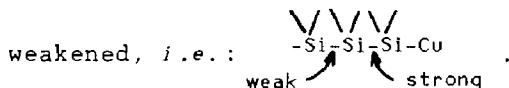
The reaction between methyl chloride and pure silicon will only proceed after a lengthy induction period (>2000 minutes at 670,695K [27]), whereas it is less than 5 minutes at 595K on Cu_3Si (Table 1).

Voorhoeve's [3f] observation that product distribution was generally independent of temperature and pressure, using a Si/Cu alloy, suggested that product selectivity was an innate function of the active catalyst, the η -phase. Just why copper in the form of an alloy with silicon is so effective as a catalyst produced many responses, e.g. those of Rochow and Hurd [23], Trambouze [17], Bažant [7,14,15], Klebansky and Fikhtengolts [22] and others [3d,11,16].

Gorbunov and coworkers studied the kinetics for the reaction of hydrogen chloride and methyl chloride with single crystals of silicon alloyed with various amounts of copper (see Table 5) [73]. When no definite correlation between copper content in the silicon and kinetic character was found, Gorbunov looked to the physical and mechanical properties of the contact mass for an explanation of the catalytic effect of the copper. Microhardness decreased significantly with copper in the range of concentrations 10^{17} to 10^{20} atoms.cm⁻³; these

results were correlated with known parallel variation of microhardness and specific surface energies of semiconductor crystals. The decrease in the specific surface energy of the crystal was a result of the decrease in the M-M surface bond strength. The selective synthesis of DMDC requires additional electronic changes associated directly with the presence of copper.

A decrease in M-M bond strength was first suggested as early as 1959 to explain the catalytic activity of copper in the synthesis of chloropolysilanes from the copper catalysed reaction of silicon metal with hydrogen chloride [74]. It was proposed that owing to the Si-Cu bond, electron density distribution was altered such that the nearby Si-Si bond was



Terakura showed from *ab initio* calculations that the *d* band of copper is capable of modifying the valence electronic states of silicon (and other metals) by hybridisation of valence *s* and *p* electrons of silicon with the *d* band of copper [75]. This view was later confirmed by Hiraki and coworkers [76] using AES, who found that when silicon is dissolved in copper with its filled *d* band, the valence electrons of silicon undergo a fundamental and dramatic change.

Cros and coworkers studied surface oxidation of Si(111) covered with a layer of gold [77a]. From the growth of SiO₂ they concluded that in the presence of gold, there was a change in the hybridisation of silicon as a result of a more metallic environment. The adsorption of silver and copper on Si(111) surfaces has been modelled and it was found that Si interacts more with Cu than Ag suggesting that in the absence of Ag activity, the catalytic activity of copper is due to its ability to diffuse to the surface and form catalytically active silicides [77b].

In light of the above, Frank and Falconer [67] proposed that the presence of copper results in the weakening of silicon bonding and so silicon may react with methyl chloride and products formed on the surface may migrate into the gas phase. The copper-silicon bond energy has been calculated to be *ca.*

126 kJ.mol⁻¹, 84 kJ.mol⁻¹ less than the Si-Si bond energy [70].

Where the bond M-Cl (M is the catalyst) is stronger than Si-Cl (382.2 kJ.mol⁻¹), for example when M is calcium (432.6 kJ.mol⁻¹), the Cl:Si ratio in the primary product decreases; for M=Ca, the primary product is trimethylchlorosilane. The decrease in the Cl:Si ratio has been interpreted in terms of strongly bound surface chlorine being less likely to be involved in reaction to form methylchlorosilanes [28]. This suggestion appears borne out by those catalysts whose M-Cl bonds are weaker than Si-Cl; when these catalysts are used the primary product contains >1 chlorine atom. However there is no correlation between such catalysts (e.g. Pb, Cu, Sn, and Fe) and the number of chlorine atoms found in the principal product. Falconer suggests that these catalysts may stabilise the adsorbed methyl group, which would serve to affect the primary product composition [28].

The oxidation state of the active copper catalyst has recently been investigated. Gupta *et al.*, using a ferrosilicon (≈4 wt% Fe) and CuCl contact mass, employed X-ray photoelectron spectroscopy (XPS/ESCA) to monitor the contact mass before and after reaction with methyl chloride (20% silicon conversion) [54]. They found strong shake-up peaks in the Cu 2p spectrum at 30Å beneath the surface which are associated with Cu²⁺; the latter were absent in the starting contact mass. Calculation of 'shake-up' with respect to the main Cu 2p peak gives a value of 0.18, indicating bonding of copper to a weakly electronegative element (neither oxygen nor chlorine). This result was believed to favour the ionic mechanism proposed by Klebansky and Fikhtengolts [22] (to be discussed).

Gentle and Owen used silicon-copper alloys and mixtures (taking care not to expose the contact masses to air) and monitored the Cu 2p region with XPS after reaction with methyl chloride in a laboratory microreactor and fluid bed reactor [55]. Unlike Sharma and Gupta [54], they found no satellite shake-up peaks indicative of Cu²⁺. Their spectra indicated for all samples used that the Cu₃Si phase was present, and the absence of shake-up peaks demonstrated that copper was present

in the zero oxidation state. Further confirmation of this conclusion was obtained by analysing the L_3VV (L_3 shell-valence-valence) Auger transition using the Wagner Method. Plotting the L_3VV kinetic energy against Cu $2p_{3/2}$ binding energy, the change in the Cu $2p_{3/2}$ energy for the four alloyed samples used agreed with data for elemental copper. The formation of Cu^{2+} shake-up peaks seen by Gupta and Sharma were explained by the presence of oxygen which resulted from exposure of their contact mass to air prior to surface analysis. Banholzer and Burrell found similar results using XPS and AES [67b,69].

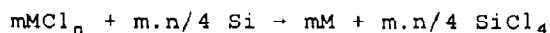
METAL CHLORIDE PROMOTERS

De Cooker *et al.* have investigated the reaction of metal chlorides with silicon and their effect on the DS [78]. These authors demonstrated that the threshold temperature of the reaction between silicon and the metal chloride, and the catalytic activity of the metal can be related by the equation

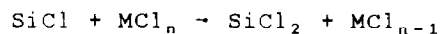
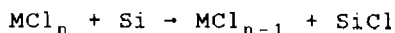
$$T_s(^{\circ}C) = 194.3 - 0.0072 \times \{\Delta G^{\circ}/Cl\} \times T_{1mm}(K).$$

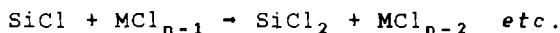
{ $\Delta G^{\circ}/Cl$ } = av. standard free enthalpy of formation/ g. at. chloride bound to metal; $T_s(^{\circ}C)$ = threshold temperature; $T_{1mm}(K)$ = temperature where vapour pressure of the metal chloride is 1mmHg.}

Whilst $\Delta G < 0$ is a criterion for reaction between the metal chloride and silicon, it is no guarantee of reaction under the conditions of the DS. The reaction can be qualitatively expressed as:



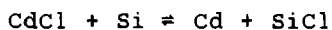
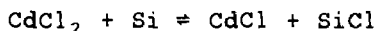
Each step in this reaction should be kinetically possible to ensure a suitable rate of reaction, *i.e.*:





Where M is copper, copper(I) chloride acts as a surface intermediate and reaction initiator [2,16,79,80] by chlorinating silicon, thereby forming surface SiCl_n species (see later).

In those cases where chlorine transfer cannot occur at every reaction step, the metal chloride may still exert an influence on the DS. If after chlorine transfer during the initial reaction steps there is a suitable decrease in free enthalpy, then these metal chlorides may act as promoters, *i.e.*:



Examples of promoters acting in this way are ZnCl_2 , AlCl_3 , and SbCl_3 [78]. The increase in reaction rate as a result of the promoter AlCl_3 , prompted Müller [81] to declare that copper was not effective enough on its own in the reaction between methyl chloride and silicon: AlCl_3 was required. Cadmium chloride is an interesting example as it can act both as a powerful promoter and also under suitable conditions, as a catalyst [78]. Between 700 and 800K the sign of ΔG_f changes from positive to negative for the reaction between CdCl_2 and silicon, and at 753K CdCl_2 reacts with silicon. Thus at lower temperatures CdCl_2 acts as a promoter, whereas at higher temperatures (>723K) it becomes a catalyst.

Promoters assist in the transfer of chlorine to silicon. In a Cu_3Si grain it is silicon which diffuses to the surface and reacts with methyl chloride. Diffusion will not be hindered by any promoters because the Cu_3Si phase is free of impurities. Impurities form structural components at the Cu_3Si grain boundaries, where reaction with methyl chloride occurs and where chlorine transfer is required [56].

Increasing the proportion of ZnCl_2 in a Si/Cu alloy contact mass (using a fluidised and rotary reactor) increases

the amount of methane formed, corresponding to a decrease of the Me:Si ratio of the products [82]. This increase prompted the suggestion that $ZnCl_2$ (<2%) increases methyl chloride decomposition. Increasing the amount of $ZnCl_2$ increases the complexity of the product mixture; this composition can be improved (to yield more DMDC) by the addition of other metal chlorides: calcium, magnesium, and potassium chlorides. Eutectic mixtures of these metal chlorides with $ZnCl_2$ make the Me:Si ratio insensitive to zinc chloride concentrations, promoting DMDC formation. Such a favourable influence results from the improved conditions of heat transfer because these eutectic mixtures have lower melting points than zinc chloride.

KINETICS AND MECHANISM

Kinetic Studies

Much of the early work into the kinetics of the DS did not take into account the profound effect of impurities, with the result that much of this work is unreliable [11] (see for example Table 2).

TABLE 2
Kinetic Parameters for DMDC Formation

No.	Contact Mass Si+Cu(9:1)	Pressure (atm)	Reaction order nMeCl	Activation Energy $kJ.mol^{-1}$
1.	Mixed powdered Si(99.9%)+Cu	0.1-0.6	1	106.3
2.	Mixed powdered Si(98%)+Cu	1-7	1	84.4
3.	Mixed powdered Si(99%)+Cu (from $CuCl$)	1	1	111.7
4.	Mixed powdered Si(99.98%)+Cu with added Al+ Zn	4.6-12.7	1	108.4
5.	Mixed powdered Si+Cu		4	84
6.	Mixed powdered Si(99%)+Cu	1	1.85	37.8

[Source: ref. 11, for individual refs. for these figures, see p. 294 of ref. 11]

TABLE 3
Apparent Activation Energies for Chlorosilane Formation
on Si(100) During Steady State Conditions

Compound	E/ kJ.mol ⁻¹
HSiCl ₃	46.2±4.2
CH ₃ HSiCl ₂	113.4±8.4
SiCl ₄	88.2±6.8
CH ₃ SiCl ₃	100.8±8.4
CH ₃ Cl	58.8±12.6
Non-silanes	46.2±16.8

[Source: ref. 21]

Frank and Falconer have studied chlorosilane production from the reaction of methyl chloride with Si(100). For steady state reaction between 545 and 620K, activation energies reported are shown in Table 3 [21]. From areal reaction rates [27], reaction of Cu₃Si is an order of magnitude slower than on Si(100); 0.56x10¹⁴ and 16x10¹⁴ Si atoms.cm⁻².s⁻¹ respectively at 545K for total methylchlorosilane formation (selectivity for DMDC was however much greater on Cu₃Si).

Falconer and coworkers [26,27] have also studied the kinetics of formation of methylchlorosilanes on a Cu₃Si alloy, with and without the promoter zinc (see Table 4).

TABLE 4
Apparent Activation Energies (kJ.mol⁻¹) for Cu₃Si Contact Masses
Containing Zinc

Product	Bulk Zn Concentration		
	(520-595K) 1.2%	(520-620K) 0.4%	(520-620K) 0%
MeCl Consumption	71.4±4.2	-	-
Me ₂ SiCl ₂	50.4±4.2	84±12.6	130.2±12.6
MeSiCl ₃	84±4.2	134.4±12.6	88.2±12.6
Me ₃ SiCl	63±4.2	-	-
Nonsilanes	96.6±4.2	-	-

[Source: ref. 26]

On Cu₃Si-Zn (0.4 to 1.2% Zn) contact masses DMDC was formed in a steady state in advance of MeSiCl₃ and Me₃SiCl [26]. Once the latter two products were formed in a steady

state, kinetics for DMDC formation showed no change suggesting that DMDC formation creates sites for MeSiCl_3 and Me_3SiCl production.

From the above table the apparent activation energy on the Cu_3Si phase is greater for DMDC formation than MeSiCl_3 formation, demonstrating that the selectivity for DMDC increases with increasing temperature. The converse is true for DMDC formation on a $\text{Cu}_3\text{Si-Zn}$ contact mass where selectivity for DMDC decreases with increasing temperatures.

Using a contact mass containing tin and zinc (1.5% Cu, 1000ppm Sn/Cu and Zn/Cu = 0.1), which together show a synergistic effect, an activation energy for methyl chloride consumption (20% silicon utilisation) of $124.3 \text{ kJ.mol}^{-1}$ was reported [12].

Not only have researchers been interested in the steady state reaction and the effect of bulk diffusion within the contact mass [27], but the induction period has also been modelled. Falconer has proposed the following model for the induction period, where the reaction order $n = 0$ or 1:

$$M = \text{const.} \exp \left[\frac{E_S - E_N}{RT} \right]$$

{ M = monolayers reacted during induction; E_S = activation energy for site formation (estimated = $155.4 \pm 29.4 \text{ kJ.mol}^{-1}$); E_N = activation energy for reaction ($138.6 \pm 8.4 \text{ kJ.mol}^{-1}$ on Cu_3Si)}

Similar values for E_S and E_N (*vide supra*) indicate that the rate determining steps (RDS) are common to both active site and product formation and those steps leading to product formation are non-rate-limiting (desorption, for example). Hence, copper and zinc have smaller induction periods owing to an increase in rate of production of active sites [27]. A value of $92.4 \pm 8.4 \text{ kJ.mol}^{-1}$ for the induction period resulting from the breakdown of ethyl chloride on a Si/Cu alloy contact mass containing free silicon has been reported [29].

From static experiments following pressure changes, Bažant [14,15] formulated the following equation:

$$r = \frac{kK_A p_A}{[1 + \sqrt{(K_A p_A) + K_R p_R}]^2}$$

{r = reaction rate, mole.h⁻¹.kg⁻¹; k = rate constant, mol.h⁻¹.kg⁻¹; K_A, K_R = adsorption coefficient, atm⁻¹: A = MeCl and R = silanes; p = partial pressure, atm⁻¹}

This equation is also applicable to the DS under high pressure in a flow system [14]. Experimental kinetic data are consistent with a first order dependence on methyl chloride [83]. So for low percentage conversion of methyl chloride and low temperatures the term (K_Ap_A)^{1/2} can be ignored. This term represents the deactivation of the contact mass with increase in temperature as the organic group of the alkyl chloride starts to undergo thermolysis [11]. The above equation predicts the RDS to be in the monolayer after dissociative adsorption of the alkyl chloride [7,14]; this is something which will be discussed later.

TABLE 5
Effect of Increase In Copper Content of Contact Mass

Copper content wt, %	Reaction order, ⁿ HCl	Activation Energy kJ.mol ⁻¹
0.0	0	142
0.0013		113.4
0.005	0.27	120.5
0.04	0.65	100.8
0.08	0.22	136.3
0.3	0.54	103

[Source: ref. 73]

Gorbunov *et al.* [73] studying the reaction of silicon with hydrogen chloride on single crystals of silicon alloyed with low concentrations of copper (see Table 5), found no definite correlation of copper content in the silicon with activation energy E or order with respect to hydrogen chloride, *i.e.* [HCl]ⁿ. Voorhoeve also commented on the effect of increasing the copper content, where changes in copper content did not cause parallel changes in the rate of reaction; above a certain concentration the rates were affected because copper now

occupied an increased proportion of surface active sites [3e]. In addition, it was discovered that in a fluidised-bed reactor the activation energy was not significantly affected by pressure (Table 6) [3b]. At pressures between 4 and 26 atmospheres methylchlorosilane production followed neither first nor second order kinetics but did seem to fit Bažant's equation (above), again suggesting that the innate properties of the contact mixture controlled this reacting system.

TABLE 6
Effect of Pressure on E (Fluidised-bed Reactor)

Pressure (atm)	Activation Energy kJ.mol ⁻¹
1	111.7
3	130.0
4.6	108.4
12.7	108.4

[Source: ref. 3b]

Bažant's equation has been modified [66] to include the effect of change in silicon conversion in Cu₃Si, to produce:-

$$R_v = \frac{k}{(C_{Si\eta})_o^2} \cdot \frac{C_{Si\eta}^2 K_A p_A}{[1 + \sqrt{(K_A p_A)}]^2}$$

{ R_v = rate of reaction of silicon, (gmol silicon).cm⁻³ η-phase.s⁻¹; k = reaction rate constant, gmol silicon.cm⁻³ η-phase.s⁻¹; $C_{Si\eta}$ = concentration of silicon in the η-phase, gmol.cm⁻³ [($C_{Si\eta}$)_o = initial value]; K_A = adsorption equilibrium coefficient for methyl chloride, atm⁻¹; p_A = partial pressure of methyl chloride, atm.}

leading to:

$$k = 2.3 \times 10^6 \exp\left\{\frac{-13085.0}{T}\right\} \left[\frac{\text{g mole Si}}{(\text{cm}^2 \text{ of } \eta) (\text{s})} \right]$$

Ward *et al.* working with fluidised and stirred bed reactors produced an interesting rate constant k_p (g silane.h⁻¹, g silicon), which is independent of amount of

silicon present and methyl chloride flow rate. k_p is defined by the following equation [12]:

$$k_p = \frac{4.6F (I-II-III)}{2K_A M_{Si}}$$

where:

$$I = \left[\frac{1}{2P} - K_B + \frac{PK_B^2}{2} \right] X ;$$

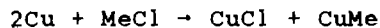
$$II = \left[\frac{1}{2P} + K_B + \frac{PK_B^2}{2} \right] \log (1-X) ;$$

$$III = 2PK_B^2 \log \left[1 - \frac{X}{2} \right].$$

{ k_p = reaction rate constant, g silane/g Si,h; F = MeCl feed flow, moles/h; $K_{A,B}$ = adsorption equilibrium constants (A=MeCl, B=silane); M_{Si} = Si in reactor, moles; p = total reactor pressure, atm.; X = fraction of MeCl conversion.}

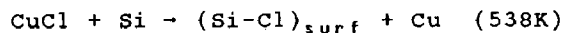
Mechanism of the Direct Synthesis

The first mechanism proposed to account for the formation of organohalosilanes was that proposed by Rochow and Hurd [23] in 1945, who concluded that the purpose of the copper was to transport the halogen from the alkyl chloride (as copper(I) chloride) and make the methyl group available to silicon in the form of methylcopper. The copper(I) chloride and methylcopper were to be formed in the following process:

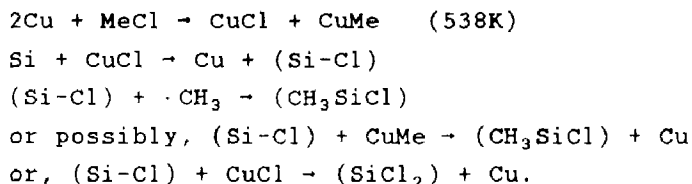


(average lifetime of CuMe: 0.003-0.005 secs. at 523K).

Copper(I) chloride is subsequently reduced by elemental silicon (at 538K) in a highly exothermic reaction to give (Si-Cl) and Cu (thereby maintaining the status of copper as a catalyst), *i.e.*:



The decomposition of methyl copper leads to the formation of methyl radicals and subsequently to the methylation of silicon. In full, Hurd and Rochow proposed the following scheme:



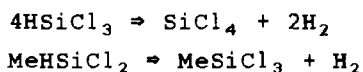
The chlorinated intermediates remain on the surface of the silicon. The purpose of the (Si-Cl) intermediate is that by chlorinating the silicon, it is activated to such a state that it is able to become methylated to give DMDC selectively. It should be noted that for this sequence of reactions it is necessary only for silicon and copper to be in close contact and not alloyed.

The intermediacy of methylcopper was questioned when Müller found no evidence for it in the reaction of copper with methyl chloride [84]. In addition, this mechanism has been severely criticised by the early workers in this field: see in particular Voorhoeve and Vlugter [39]. The involvement of radicals in the formation of DMDC has been rejected [3d,11,14,15] by the use of radical initiators and inhibitors. From experiments involving nitric oxide (NO), a radical acceptor [3d,15], free methyl radicals are not believed to be involved in the formation of methylchlorosilanes. Instead, from the agreement found between critical NO:MeCl ratios (that ratio where synthesis is inhibited) and the fraction of methyl chloride forming decomposition products (e.g. hydrocarbons), Bažant [15] concluded there are two types of methyl group involved in the DS. One type is free methyl radicals which give rise to decomposition products, whereas the second, which gives rise to methylchlorosilanes, is associated with the surface of the contact mass. Voorhoeve has pointed out that there is no evidence that the added NO does not reduce the

reaction rate by catalytic poisoning, or combining with $\cdot\text{CH}_3$ radicals that form methylchlorosilanes [3d].

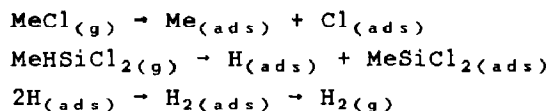
Voorhoeve reports further experiments involving azomethane (MeN=NMe), a source of methyl radicals [3d]. A partial pressure of 10 mmHg of azomethane halves the reaction rate and DMDC falls from 89 to 82%. On increase of the partial pressure beyond 10 mmHg, methylchlorosilane production ceases. When the flow of azomethane is stopped, methylchlorosilane production resumes. It was concluded therefore that methyl radicals are not involved in methylchlorosilane production.

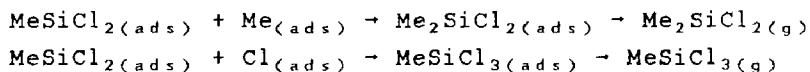
It has been shown by generating methyl radicals (generated from the thermolysis of Me_2Hg at 723K) in the presence of hydridochlorosilanes, that the Si-H bond is very reactive towards methyl radicals compared to the C-H bond [62]. Abstraction of hydrogen from the Si-H bond in HSiCl_3 results in the formation of SiCl_4 together with more complex products. Similarly, reacting MeHSiCl_2 with methyl radicals results in the formation of MeSiCl_3 ; that is, for both cases:



The ease with which H is abstracted by methyl radicals is inconsistent with the original radical mechanism of Hurd and Rochow [23] as such reactivity should exclude significant formation of the compounds, HSiCl_3 and MeHSiCl_2 , during the DS but is consistent with a homogeneous mechanism, allying itself more with a heterogeneous one.

In additional experiments [61], MeHSiCl_2 was added to the methyl chloride flow over a Si/Cu alloy which favoured the transformation of MeHSiCl_2 to MeSiCl_3 and DMDC. The large amount of hydrogen formed (representing 67% of MeHSiCl_2 added) suggested that the hydrogen came from MeHSiCl_2 which was explained by the following heterogeneous scheme:





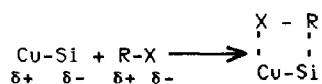
Rochow and Hurd [23] proposed a heterogeneous-homogeneous mechanism, with methylcopper and copper chloride being formed on the surface and migrating into the gas phase. Owing to the inadequacies of their mechanism and the moderate successes of others (e.g. Klebansky and Fikhtengolts, below), researchers began to look at the DS as a heterogeneous process.

Chemisorption Mechanisms

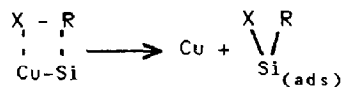
The onus on any mechanism is to account for the high selectivity of the DS for DMDC, and account for the formation of a particular alloy of silicon and copper, namely the Cu_3Si phase. The first step of a heterogeneous mechanism involves the chemisorption of methyl chloride onto the contact mass. Mechanisms were proposed explaining the selective formation of DMDC during initial adsorption of methyl chloride. Such mechanisms were proposed in the 1950's: first by Trambouze [17], then by Klebansky and Fikhtengolts [22] (later to be extended by Voorhoeve [3d] and coworkers [39]), and Bažant and coworkers [14,15].

The chemisorption mechanisms all assumed dissociative adsorption of methyl chloride as the first step. To incorporate the need for specificity during adsorption, workers looked carefully at the ionic properties of the alkyl chloride and the surface of the contact mass. One thing became clear, the need for alternating the silicon and copper on the solid surface and hence the mechanistic need for a Si/Cu alloy, *viz.* Cu_3Si .

Klebansky and Fikhtengolts proposed a mechanism where they suggested that the adsorption of methyl chloride on the surface is controlled by the dipole moment and charge distribution in the alkyl chloride and contact mixture respectively [22]; diagrammatically:

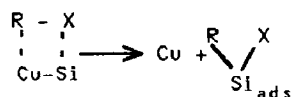


followed by rearrangement to give the following:



The above mechanism predicts the selective formation of DMDC as it requires R and X to be in the immediate vicinity of the reacting silicon, thus ensuring an even number of R and X groups in the product.

Bažant and coworker [85], and Trambouze [17] proposed a similar mechanism where RX dissociatively adsorbs onto the alternate Si-Cu surface of the alloy to give DMDC. The difference between this mechanism and that of Klebansky and Fikhtengolts' above, is that Bažant and Trambouze believe adsorption of RX occurs in the reverse fashion, *i.e.*:



with the electrophilic transfer of R from copper to silicon. The proponents of this mode of adsorption believe that the rate enhancement seen with methyl bromide is proof of this mechanism, as Br is not as electron withdrawing as Cl. It would therefore be expected that the activation energy for reaction between a Si/Cu contact mass and methyl bromide would be less than that for the reaction with methyl chloride [3d]. In fact, the activation energy for reaction of the Si/Cu contact mass with methyl chloride is 106.3 kJ.mol⁻¹ and with methyl bromide it is 155.4 kJ.mol⁻¹; this is judged not to be reconcilable with Bažant's mechanism [3d,39].

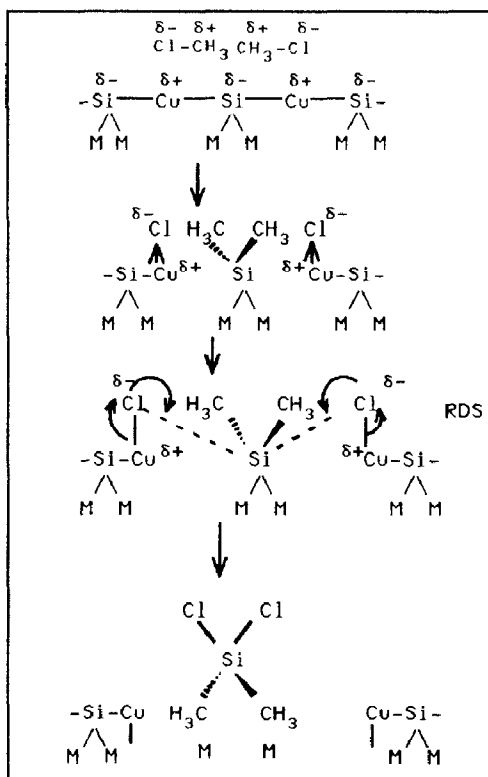
Further evidence in favour of the Klebansky-Fikhtengolts mechanism came from work involving silicides [3d,39]. This work favoured the ionic mechanism and suggested the polarisation of the Si-Cu surface to be -Cu^{δ+}-Si^{δ-}; this is

consistent with recent AES experiments (the partial charges have been calculated to be $\text{Cu}^{\delta+}=0.017$ and $\text{Si}^{\delta-}=0.052$) [70]. Taking into account the electron density in Ca, Cr, and Fe, and the selectivities found, the following table was constructed [3d,39]:

TABLE 7
Charge Distribution in Metal Silicides

Silicides, in order of increased electronegativity of metal	Partial Charge Distribution		Main Product(s)
	Metal	Silicon	
Ca-Si	+	-	Me_3SiCl Me_2SiCl_2 $\text{Me}_2\text{SiCl}_2 + \text{MeSiCl}_3$ MeSiCl_3
Cu-Si	+	-	
Cr-Si	0	0	
Fe-Si	-	+	

[Source: refs. 3 and 39]



[Source: ref. 3d]

With these data Voorhoeve and Vlugter [3d,39] proposed the above scheme which is an extension of the Klebansky-Fikhtengolts mechanism, where two physically adsorbed molecules of methyl chloride are adsorbed in accordance with the polarity of the surface and RX. As physical adsorption leads to chemisorption, reaction on the surface takes place to give products.

Regarding the nucleophilicity of the RDS, it can be appreciated that those factors which increase the electron density on the silicon atom will decrease the reaction rate. The Cu-X bond strength affects the activation energy as it must be broken before reaction.

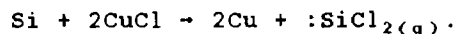
The above mechanisms have been criticised because they make no allowance for the active surface which contains chlorine and carbon deposits as well as copper and silicon [28]. The formation of Si-Cl active sites [21,28] cannot be accounted for nor incorporated into the above chemisorption mechanism.

Chlorinated Intermediates

There has been a great deal of effort put into the identification of intermediate silicon-chlorine compounds, in particular by Golubtsov [35,45-51,86], and others [14,16,21-24,27,87].

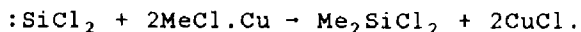
Falconer and coworkers have been the most recent group to show the intermediacy of chlorine bound to silicon [21,27]. Using AES they showed that active sites in the formation of DMDC are surface-bound (Si-Cl) species.

It has been suggested that dichlorosilylene (:SiCl₂), is formed by the chlorination of silicon with copper(I) chloride (453K) [48]:



The silylene is then envisaged to react with methyl chloride adsorbed on the copper, regenerating copper(I) chloride in the

formation of products [48]:



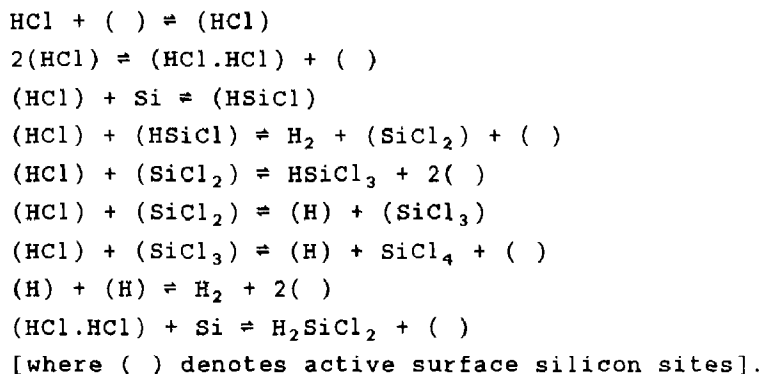
The formation of $:\text{SiCl}_2$ in the gas phase is conceivable if the effect of copper is to weaken silicon-silicon bonding.

In addition, evidence was obtained for the formation of $:\text{SiCl}_2$ in the reaction between silicon and copper(I) chloride in experiments carried out in the ion source of a mass spectrometer [48]. The contact mixture was a 3:8 (by weight) mixture of copper(I) chloride and silicon which upon heating produced tetrachlorosilane. Comparing the intensity of ion fragments in the mass spectrum from products of reaction with that of an authentic spectrum of tetrachlorosilane, it could be seen that the relative intensities, (I/I_{133}) , [$m/e=133 \equiv \text{SiCl}_3^+$] of the fragments produced with the exception of fragments with $m/e = 98^+$ and 100^+ (corresponding to $^{28}\text{Si}^{35}\text{Cl}_2^+$ and $^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$) were the same. (I_{98}/I_{133}) resulting from the reaction of copper(I) chloride with silicon was more than six times greater than the ratio found under identical conditions for tetrachlorosilane ($I_{98}/I_{133} = 0.161$ and $I_{100}/I_{133} = 0.106$ from reaction products, $I_{98}/I_{133} = 0.024$ and $I_{100}/I_{133} = 0.016$ for SiCl_4).

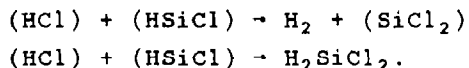
Additional information concerning the formation of $:\text{SiCl}_2$ (experiments were carried out in the ion source of a mass spectrometer) was produced from the reaction of hydrogen chloride with silicon [49]. Ion currents were recorded for SiCl^+ , SiCl_2^+ , and SiCl_3^+ (i.e. m/e : 63, 65, 98, 100, and 133). Comparing the ion currents which resulted from HSiCl_3 (the principal product of the reaction between silicon and HCl), $:\text{SiCl}_2$ was concluded to be formed on the surface and desorbed into the gas phase. It was suggested that the ions SiCl^+ and SiCl_3^+ may result from independent intermediates as well as being ion fragments of some minor reaction products. It is not clear whether the ion current for SiCl (m/e : 63 and 65) was also the result of the loss of H from HSiCl . It is not unreasonable to postulate the formation of HSiCl in a system where $:\text{SiCl}_2$ is believed to be present, especially when the

reacting gas is hydrogen chloride.

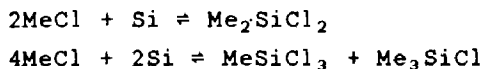
Chlorosilylene (HSiCl) has been suggested as an intermediate in the reaction between silicon and hydrogen chloride. Filippov and coworkers attempted to explain the synthesis of trichlorosilane and the selectivity for dichlorosilane produced by the reaction of hydrogen chloride (400-450 mmHg) in a circulatory-static system using silicon (99.9999% pure) with 5% CuCl [88]. A nine stage mechanism comprising six surface intermediates was proposed as follows:

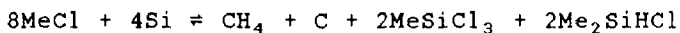
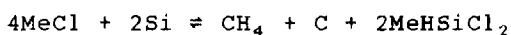


The authors remark that (SiCl₃) [an intermediate in the formation of SiCl₄] requires experimental verification. The authors agreed with earlier work [35] that the formation of an intermediate species could result in selective formation of a product. In this scheme selectivity was achieved between adsorbed molecules of hydrogen chloride and (HSiCl), *i.e.*:



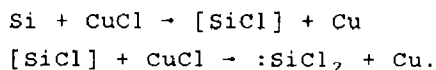
Gorbunov *et al.* [89] modelled the reaction between silicon and methyl chloride. Their mechanism predicted eight independent intermediates involving twelve reaction steps. For such a condition the following four pathways are predicted:





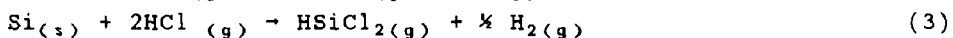
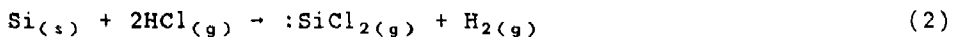
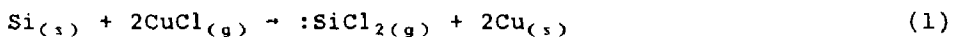
In addition to the formation of $:\text{SiCl}_2$ from the reaction of copper(I) chloride and silicon [48], other chlorinated intermediates have been proposed from experiments performed in the modified ion sources of two mass spectrometers to monitor intermediates of reaction [50]. Appearance potentials of ions were measured in one spectrometer where the resulting product fragmentation was achieved by electron impact. In the second spectrometer, fragmentation was achieved by photoionisation. The principal product of the reaction between copper(I) chloride and silicon was tetrachlorosilane. By comparing the appearance potentials for SiCl_4^+ , SiCl_3^+ , SiCl_2^+ , and SiCl^+ fragments with those for an authentic sample of tetrachlorosilane (fragments were generated by electron impact and photoionisation), it was concluded that in addition to $:\text{SiCl}_2$, the intermediates SiCl_3 , and SiCl were formed; under the experimental conditions these intermediates desorb into the gas phase.

The theme of reactive intermediates was taken further in an article by Golubtsov *et al.* [35] in which the role of copper(I) chloride was discussed. As above, the formation of $:\text{SiCl}_2$ is the result of chlorination of silicon by copper(I) chloride through the formation of the intermediate, $[\text{SiCl}]$:

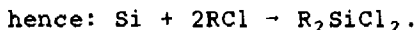
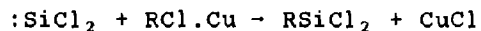
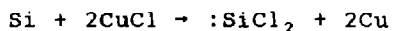
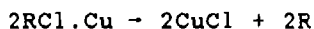
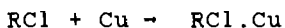


Earlier, Golubtsov [38] mentioned that the concentration of copper(I) chloride in the reaction zone was so important that it determined the R_2SiX_2 content of the products.

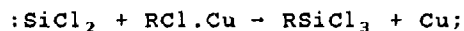
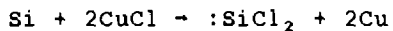
Golubtsov [35] investigated the possible products of partial chlorination or hydrochlorination of silicon under the conditions of the DS by calculating equilibrium constants (K_{eq}) for a group of six possible reactions involving intermediate species; concluding that the following reactions were theoretically possible:



Calculation of K_{eq} between 500 and 600K revealed that the formation of :SiCl_2 could be considered preferential; reaction (1) above showed the greatest change over the temperature range studied. In addition to this study, UV absorption spectra of the reaction products of copper(I) chloride and silicon (principally tetrachlorosilane) gave evidence for what was believed to be :SiCl_2 , assigning the absorption as 315nm. The following scheme was proposed [35,38]:



To account for the formation of RSiCl_3 :



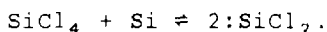
which does not regenerate copper(I) chloride.

The role conferred on R and RSiCl_2 is not clear from this mechanism. There is a great deal of evidence for R radicals [3d,11,13,14] but not for RSiCl_2 in the gas phase. The combination of two MeSiCl_2 units to form $\text{MeCl}_2\text{SiSiCl}_2\text{Me}$ is a feature of the surface chain mechanism [2] discussed later. The use of radical initiators and inhibitors (see earlier) suggests that if species of this type are formed then they are to be regarded as surface compounds.

Data collected on the DS confirm parts of this mechanism but not others. The formation of $[\text{SiCl}]$ surface intermediates was confirmed by Falconer and coworkers [21,27], but starting

from Cu_3Si copper(I) chloride was not observed and neither was tetrachlorosilane a prominent product. These points do not disprove the formation of $:\text{SiCl}_2$, as data collected later concerning the bonding in silicon-copper alloys, suggests the likelihood of silicon release from the surface (see above, 'Role of Copper as Catalyst').

Heating silicon and copper(I) chloride together ($\approx 573\text{K}$) produces principally tetrachlorosilane and some hexachlorodisilane [43,48,60,68] (plus Si_3Cl_8) [78]. Tetrachlorosilane, a product of chlorinated silicon, has been suggested to be the product of secondary transformations of partially chlorinated surface intermediates [90]. The formation of tetrachlorosilane from dichlorosilylene by the following process has been noted [35,48]:

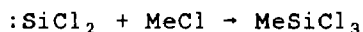


The above reaction has been used to successfully generate $:\text{SiCl}_2$ at temperatures greater than 1273K [91-94]. It seems plausible to suggest that $:\text{SiCl}_2$ may be generated at a temperature less than 1273K if copper is present, in the case of copper(I) chloride and silicon mixtures as demonstrated by Zubkov [48] for instance. The formation of hexachlorodisilane [43] could then be explained by the insertion of $:\text{SiCl}_2$ into the Si-Cl bond of tetrachlorosilane [95,96], Si_3Cl_8 being the product of insertion into the Si-Cl bond of Si_2Cl_6 .

Popenko *et al.* [87] have more recently used equilibrium constants, K_{eq} , to explain the formation of dichlorosilane in the copper catalysed reaction of chlorinated silicon with hydrogen chloride. In their calculations they assume that there are two types of equilibrium reaction, one which occurs with $[\text{SiCl}]$ on the surface and another with chlorinated silicon intermediates SiCl_n ($n=1-3$) in the gas phase. The authors calculated K_{eq} for 29 possible chlorination reactions at seven temperatures between 298K and 900K , both on the solid surface and in the gas phase. From the equilibrium constants calculated, the authors concluded that steps which involve $\text{SiCl}_{(surf)}$, $\text{SiCl}_{(gas)}$, and $\text{SiCl}_{2(gas)}$ could account for product

distributions found.

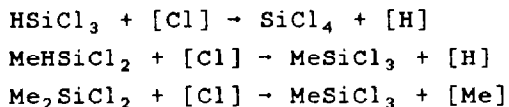
When silicon was heated in the presence of methyl chloride, trichloromethylsilane and tetrachlorosilane were produced but only at high temperatures (>773K) [51,80,90]. However prior chlorination of the surface (within a modified mass spectrometer) gave tetrachlorosilane at 563K and MeSiCl₃ at 583K, believed to be the result of the formation of SiCl_n [51]. Fluorine, being more electronegative than chlorine, results in the formation of halogenosilanes at temperatures ca. 200K below those found for hydrochlorination when the surface is heated with hydrogen fluoride. The formation of MeSiCl₃ was rationalised by the following [80]:



Heating chlorinated silicon and a silicon/copper alloy in a helium stream [80,90] gave SiCl₄ which was believed to be the result of secondary transformations of partially chlorinated intermediates, SiCl_n [80].

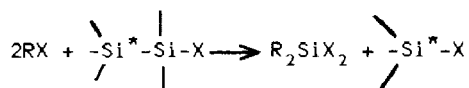
Dichlorosilylene has been shown to insert into the C-Cl bond of tetrachloromethane [93,94] to give Cl₃SiCCl₃. Thermal formation of :SiCl₂ generates the singlet state [95-97] and insertion reactions into single bonds by singlet silylenes are common (for a more detailed discussion of silylene reactions see the reviews by Gaspar [97], and Chernyshev and coworkers [96]). Methylchlorosilylene (MeSiCl) and other silylenes have been proposed as both surface and gas phase intermediates in the DS [70].

Frank and Falconer believe that in the reaction between Si(100) and methyl chloride, the surface Si-Cl sites may act as nucleophiles capable of replacing Si-H or Si-C bonds with Si-Cl bonds at higher temperatures [21]. On a chlorinated Si(100) surface they propose the following reactions:

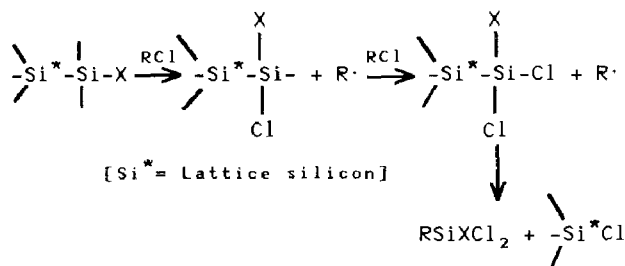


At higher temperatures, Falconer believes that such secondary chlorination reactions account for deviations from Arrhenius behaviour, suggesting that relative stability of chlorosilanes [$>670\text{K}$ on $\text{Si}(100)$] decreases in the following manner: $\text{MeSiCl}_3 > \text{SiCl}_4 > \text{MeHSiCl}_2 > \text{HSiCl}_3$.

Interesting results have been found using the fluorinating agent hydrogen fluoride [45,80]. Reacting methyl chloride with a fluorinated silicon surface gives DMDC and Me_2SiFCl as predominant products; additional products include Me_3SiF , MeSiClF_2 , Me_2SiF_2 and MeHSiFCl . Prior to halogenation of the surface R_2SiX_2 was very small. These results prompted the following scheme:



and:



By altering the chlorination procedure it was possible to alter the surface SiCl_n composition [79], indeed such variation has produced conditions whereby DMDC was formed selectively. Reacting surface SiCl_n compounds with a methyl Grignard reagent, the proportions of SiCl_n determined from the chloromethylsilane products using a Si/Cu (5% Cu) alloy were given as follows: SiCl (40-70%), SiCl_2 (0-32%), and SiCl_3 (19-40%).

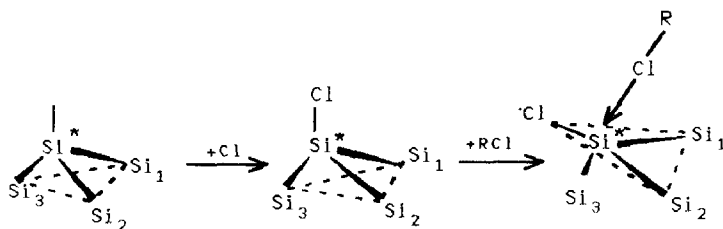
The idea that particular surface intermediates (SiCl_n) give rise to particular products, has been supported by the following results.

Prior chlorination of a silicon surface with chlorine results in the formation of predominantly MeSiCl_3 when methyl chloride is added. Using a 5% copper and silicon alloy again

treated with chlorine and then reacted with methyl chloride, predominantly DMDC was found [98]. DMDC was also a major product of the reaction of silicon (in the absence of copper) with methyl chloride after prior hydrochlorination (it is unlikely here that the silicon was pure if a significant quantity of DMDC was formed). From these results it was concluded that the intermediates SiCl_2 and SiCl_3 are formed when silicon is treated with chlorine, and SiCl when treated with hydrogen chloride, which is also preferentially formed when the Si/Cu alloy is treated with chlorine; earlier it was reported that hydrochlorination of KR-1 grade silicon resulted in dissociation of hydrogen chloride to give SiCl species (and Si-H species) [99]. In another experiment where copper powder was added to previously chlorinated silicon and reacted with methyl chloride, the DMDC yield was negligible; appearing to confirm the role of copper in chlorine transfer and promoting the formation of SiCl intermediates; SiCl_2 and SiCl_3 are formed on the silicon surface as a result of surface chlorination using chlorine [98]. These results were further confirmed by treating the surface compounds (formed by treatment of silicon or Si/Cu alloy with chlorine or hydrogen chloride) with dimethyl ether [100] between 523 and 773K. Temperatures above 623K resulted in products from reaction of dimethyl ether with SiCl_n , while no products were seen from reactions involving non-chlorinated surfaces. Products observed were Me_3SiCl , DMDC and $(\text{MeO})_2\text{SiCl}_2$, MeSiCl_3 and MeOSiCl_3 , believed to correspond to the intermediates SiCl , SiCl_2 , and SiCl_3 respectively.

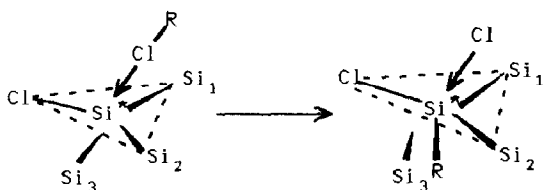
Podgornyi *et al.* suggested a possible mechanism for the formation of DMDC and trichloromethylsilane from surface-bound partially chlorinated silicon intermediates [46,47]. From surface potentials they established that the β -adsorption complex is active during the DS; they realised that $\equiv\text{SiCl}$ were active sites.

Chlorination of surface silicon results in the following:

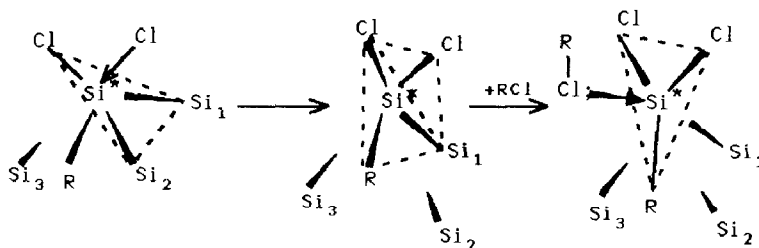


Adsorption of RCl (β form) gives a pentavalent complex and the distortion as a result of this complex, means less orbital overlap between Si* and the peripheral lattice silicons, the weakest bond being Si*-Si₃.

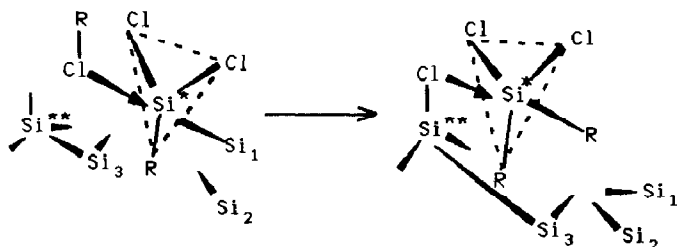
As a result of the donor-acceptor bond between Si* and the chlorine of the adsorbed RCl, the R-Cl bond is also weakened, thereby allowing the following transformation:



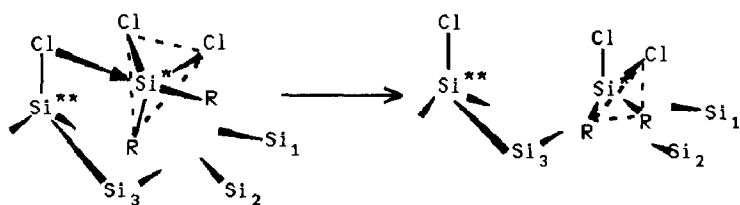
The chlorine has an unpaired electron which it uses to form a covalent bond with Si*:



Silicon, now bonded to two chlorine atoms, is more reactive thereby enabling it to form more donor-acceptor bonds with another adsorbed RCl, thus changing the coordination of the intermediate complex and resulting in further Si-Si bond weakening:



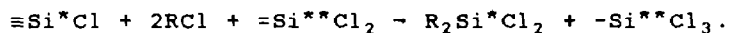
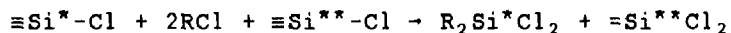
Chlorine, with its unpaired electron, forms a covalent linkage with Si^{**}. The result is a compound with two Si-C bonds which serve to reduce the stability of the hypervalent state and so form DMDC:



leaving a Si-Cl bond to perpetuate reaction. This mechanism can be summarised by the following simple equation:



Similar equations can be written for the intermediacy of =SiCl₂ and -SiCl₃, thus:-



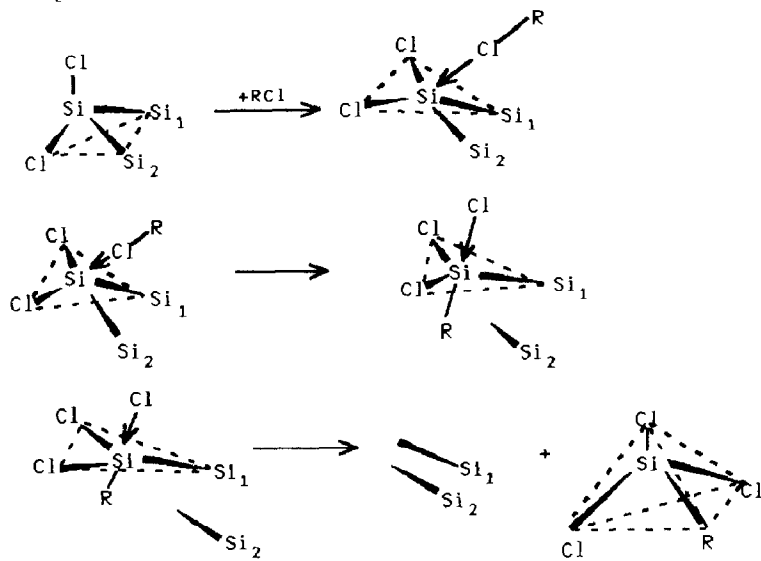
Increasing the number of chlorine atoms bound to silicon increases the donor-acceptor properties of silicon. Therefore =SiCl₂ and -SiCl₃ would be expected to react quickly, resulting in the formation of MeSiCl₃.

The formation of trichloromethylsilane involving =SiCl₂ and -SiCl₃ *via* a similar mechanism to that described above is shown in Schemes III and IV; the same principles apply.

What is not clear in these mechanisms is the role of the copper catalyst. Clearly, to produce DMDC and

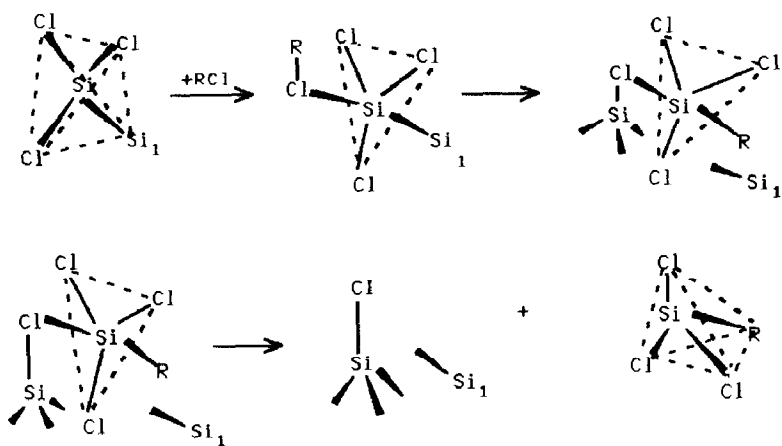
SCHEME III

[Source: ref. 46]



SCHEME IV

[Source: ref. 46]



trichloromethylsilane, more than just prior chlorination is required as the reaction between methyl chloride and silicon produces very little DMDC [21].

Banholzer, Lewis, and Ward [43] have monitored the reaction of methyl chloride with the orientated silicon wafers, Si(100) and Si(111), coated with copper(I) chloride. On Si(111) they found, using Scanning Electron Microscopy (SEM), hexagonal pits which were accompanied by irregular shaped sites, while on Si(100) square pits were observed. As reaction with methyl chloride proceeded, the Si(111) planes became exposed. The above authors concluded from experiments where they compared surfaces cleaned with Caros (1:1 hot conc. sulphuric acid and 30% hydrogen peroxide) and surfaces cleaned with Caros and 1% hydrofluoric acid, that the pits (produced as the result of methylchlorosilane formation) are formed at surface SiO₂ defects. Additional cleaning with hydrofluoric acid produced a greater density of these pits under identical conditions; chemical etching with hydrofluoric acid increased the number of SiO₂ surface defects.

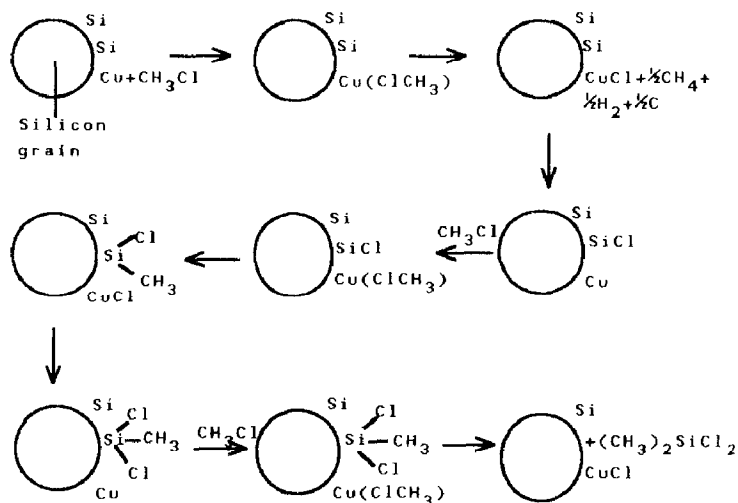
To explain the observation that the shape of the pits found by etching the silicon surface with methyl chloride differed on Si(111) and Si(100), it was concluded that one or more steps in the reaction between methyl chloride and silicon is anisotropic [43]. Comparing methyl chloride etching with crystallographic etching of silicon used by the electronics industry, etching is slow in the <111> direction where the (111) planes are exposed. Etching has been correlated to the number of 'free dangling' bonds at the surface, the more 'dangling' bonds, the faster the rate of etching; Si(111) has the lowest number of these bonds and therefore etches slowly. For this bonding idea to be the origin of the observed anisotropy, reaction must be controlled at the surface and not by diffusion.

The exposure of the (111) planes of the silicon may in addition, be the result of the reaction of copper in the <111> direction (of the silicon lattice) being limited, giving rise to this anisotropy [43]. This would be important since Banholzer *et al.* [43] believe that it is the copper (formed

from the η -phase after reaction with methyl chloride) which diffuses towards the Si/Cu₃Si boundary to form the η -phase.

It has been shown that chlorosilane formation follows Arrhenius behaviour between 545 and 620K (one atmosphere of methyl chloride over Cu₃Si) [21]. In light of such results it has been suggested that partially chlorinated intermediates involved in the formation of chlorosilanes are regenerated during reaction [16,79,80]. In this sense the DS may be regarded as having elements of a chain mechanism where chlorinating agents such as hydrogen chloride, chlorine and copper(I) chloride, act as initiators by forming SiCl_n surface compounds [16].

SCHEME V

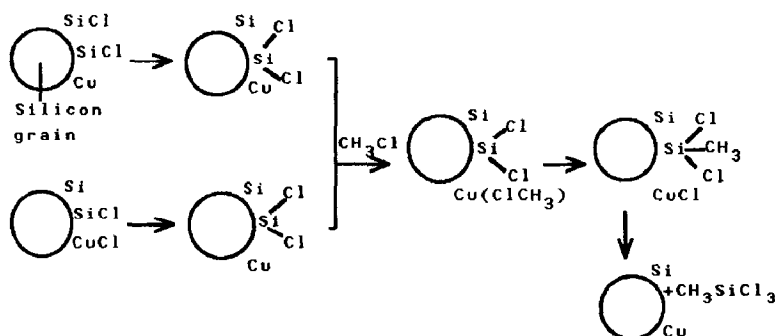


This idea of a chain mechanism lies behind the above mechanism [2,78]. The reaction between methyl chloride and silicon (in the presence of copper) is a heterogeneous one initiated at the active surface sites, Si-Cl. The catalyst in the form of copper(I) chloride effects the chlorination of silicon to form these Si-Cl active sites. Copper(I) chloride is formed by breakdown of the adduct formed when methyl chloride adsorbs on copper *via* a Langmuir type adsorption,

forming hydrogen, hydrocarbons and carbon in addition to copper(I) chloride. DMDC formation can be rationalised by continuous active site formation, as shown above.

As the Si-Cl sites are formed adjacent to the Cu.MeCl adducts, transfer of a methyl group is likely, giving surface bound ClSiMe intermediates. The chain reaction shown in Scheme V may be terminated by two events, either two neighbouring Si-Cl groups combine to give silicon plus $\text{SiCl}_2(\text{surf})$, or a neighbouring SiCl group and copper(I) chloride combine again to give surface bound SiCl_2 *i.e.*:

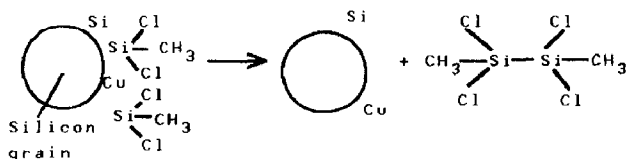
SCHEME VI



In the same way that trichloromethylsilane is formed (*vide supra*), trimethylchlorosilane formation can be envisaged by a similar route involving Si-Me surface intermediates, as opposed to the Si-Cl intermediates required for trichloromethylsilane formation.

The above mechanisms may be extended to account for dimethylchlorosilane and dichloromethylsilane formation in a similar fashion. Disilanes, *e.g.* $\text{MeCl}_2\text{SiSiCl}_2\text{Me}$, which form part of the high boiling fraction [2,18] of the DS, may be rationalised by the combination of two intermediate silicon moieties, *e.g.*:

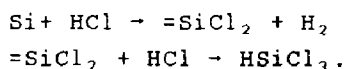
SCHEME VII



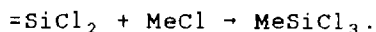
FORMATION OF DICHLOROMETHYLSILANE (DCMS)

The majority of products in the DS are monosilanes which vary in the number of methyl and chloride groups *i.e.* $\text{Me}_n\text{SiCl}_{4-n}$ ($n=1-3$). Alongside these products is MeHSiCl_2 , distinguished by the possession of a Si-H bond (Me_2HSiCl is also formed but in smaller amounts). Owing to this distinction, some research groups have made a special effort to account for DCMS formation.

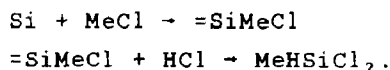
Hydrogen chloride has been used to activate the DS contact mass; this activation has been attributed to the fast and easy formation of surface Si-Cl active sites [21]. Hydrogen chloride is generally considered to be at the heart of DCMS formation. Reacting hydrogen chloride alone with a silicon contact mass, Bažant *et al.* suggested the following [101].



The addition of modest amounts of methyl chloride results in:

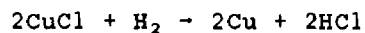


Increasing the methyl chloride content of the input gas gives:

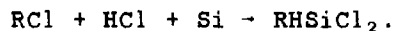


If the above sequence is true, there needs to be a pathway

by which HCl is produced during the DS. Several suggestions have come forward [3a,38,101] which involve the reduction of copper chloride formed during the DS with hydrogen formed when methyl chloride cracks on the catalytic surface:



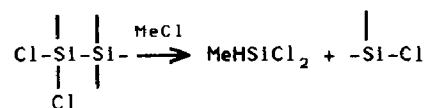
The formation of DCMS may be empirically represented as:



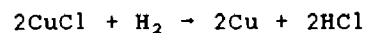
Evidence for the involvement of hydrogen chloride comes from experiments (in a static-circulation system at temperatures below 493K), where DCMS is formed at temperatures (ca. 433K) where hydrogen chloride reacts with silicon [102].

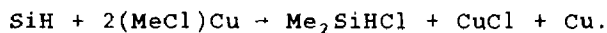
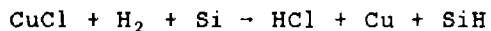
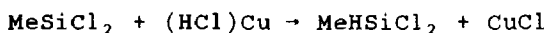
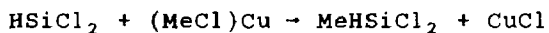
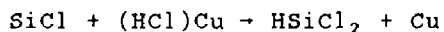
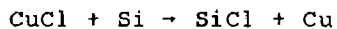
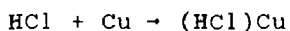
Kinetics for formation of DCMS have been reported as having an activation energy of 84 kJ.mol⁻¹ with an order of unity with respect to methyl chloride [103]. These parameters were found to be independent of the purity of silicon and the method of catalyst preparation, when using methyl and hydrogen chloride gases.

The intermediate HSiCl₂ has been suggested in the formation of DCMS, based on its proposed involvement in the reaction of hydrogen chloride with silicon [35]. Its reaction to form DCMS was formally suggested as:



DCMS (and Me₂HSiCl) can be generated with an overall selectivity of compounds containing a Si-H bond exceeding 80 mol.% by reacting methyl chloride with silicon catalysed by copper [104]. The following reactions were proposed to account for the observed products; hydrogen is required to form hydrogen chloride:-





Hydrogen has since been shown to increase DCMS content by the reduction of copper(I) chloride to give hydrogen chloride [105], or possibly by direct reaction between methyl chloride and hydrogen chloride.

One final and important point is the lack of DCMS from experiments where the contact mass consists of the Cu_3Si or $\text{Cu}_3\text{Si-Zn}(0.4\%)$ phases [26,27]; DCMS is however a major product (after HSiCl_3) in the reaction of methyl chloride with silicon [21] between 545 and 620K. The actual reason for its absence is not known, however, since hydrogen chloride is considered crucial in DCMS formation, the absence of copper (and hence any possibility of copper(I) chloride formation) may preclude its formation.

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REFERENCES

- 1 C. Hunt, *Educ. Chem.*, (1987) 7.
- 2 W. Buechner in 'Organometallic Reviews, 5th International Symposium on Organosilicon Chemistry, August 14-18 1978'. Eds. D. Seyferth, A.G. Davies, E.O. Fischer, J.F. Normant and O.A. Keutov. Elsevier, Amsterdam, 1980, p.409.
- 3 R.J.H. Voorhoeve, 'Organohalosilanes: Precursors to Silicones' 1967, Amsterdam, Elsevier; and refs. therein.

- (a) Chapter 4, p. 120ff.; (b) p. 228ff.; (c) p. 125; (d) Chapter 8, p. 244ff.; (e) p. 225; (f) p. 235.
- 4 E.G. Rochow, *J. Am. Chem. Soc.*, 67 (1945) 963.
 - 5 R. Müller, *Ger. Patent Anm.*, C57 (1942) 411.
 - 6 W.R. James, *Dissertation, Pennsylvania State College*, 1944.
 - 7 V. Bažant, J. Joklik and J. Rathousky, *Angew. Chem. Int. Ed. Engl.*, 7 (1968) 112; and refs. therein.
 - 8 C. Combes, *Compt. Rend.*, 122 (1896) 531.
 - 9 O. Ruff and K. Albert, *Ber.*, 38 (1905) 2222.
 - 10 K.M. Lewis, B. Kanner and C.C. Chang, *8th Organosilicon Symposium, St. Louis, MA.*, A39 (1987) 42.
 - 11 A.I. Gorbunov, A.P. Belyi and G.G. Filippov, *Russ. Chem. Rev.*, 43 (1974) 291; and refs. therein.
 - 12 W.J. Ward, A. Ritzer, K.M. Carroll and J.W. Flock, *J. Catal.*, 100 (1986) 240; and refs. therein.
 - 13 J.J. Zuckerman, *Adv. Inorg. Radiochem.*, VI (1964) 1383.
 - 14 V. Bažant, *Pure Appl. Chem.*, 13 (1966) 313; and refs. therein.
 - 15 V. Bažant, *Pure Appl. Chem.*, 19 (1969) 473; and refs. therein.
 - 16 R.A. Turetskaya, K.A. Andrianov, I.V. Trofimova and E.A. Chernyshev, *Russ. Chem. Rev.*, 44 (1975) 212; and refs. therein.
 - 17 P. Trambouze, *Bull. Soc. Chim. France*, (1956) 1756.
 - 18 A.N. Polinov, N.N. Troitskaya, E.V. Los', N.N. Silkina, A.S. Shepatin, M.P. Gavars, O.D. Gracheva, A.G. Trufanov and V.N. Bochkarev, *J. Gen. Chem. USSR.*, 57 (1987) 1399.
 - 19 P.J. Launer, *J. Chem. Eng. Data*, 11 (1966) 621.
 - 20 R.J.H. Voorhoeve, B.J.H. Geertsema and J.C. Vlugter, *J. Catal.*, 4 (1965) 43.
 - 21 T.C. Frank and J.L. Falconer, *Langmuir*, 1 (1985) 104.
 - 22 A.L. Klebansky and V.S. Fikhtengolts, *J. Gen. Chem. USSR.*, 27 (1957) 2693.
 - 23 D.T. Hurd and E.G. Rochow, *J. Am. Chem. Soc.*, 67 (1945) 1057.
 - 24 (a) B.H. Kolster, J.C. Vlugter and R.J.H. Voorhoeve, *Rec. Trav. Chim.*, 83 (1964) 737.

- (b) G. Weber, D. Viale, H. Souha and B. Gillot, C.R. Acad. Sci. Paris Ser. II, 307 (1988) 1155.
- 25 V.D. Krylov, R.A. Turetskaya and S.L. Lel'chuk, Russ. J. Phys. Chem., 37 (1963) 733.
- 26 J.P. Agarwala and J.L. Falconer, Int. J. Chem. Kin., 19 (1987) 519.
- 27 T.C. Frank, K.B. Kester and J.L. Falconer, J. Catal., 91 (1985) 44.
- 28 T.C. Frank, K.B. Kester and J.L. Falconer, J. Catal., 95 (1985) 396.
- 29 V.D. Krylov, Ya I. Vabel', Yu N. Efremov, A.M. Klenina and S.L. Lel'chuk, Russ. J. Phys. Chem., 33 (1959) 69.
- 30 R.A. Turetskaya, I.V. Trofimova, K.A. Andrianov and S.A. Golubtsov, J. Gen. Chem. USSR., 33 (1963) 1015.
- 31 R. Müller and H. Gumbel, Z. Anorg. Allg. Chem., 327 (1964) 286.
- 32 R.J.H. Voorhoeve, J.A. Lips and J.C. Vlugter, J. Catal., 3 (1964) 414.
- 33 R.J.H. Voorhoeve and J.C. Vlugter, J. Catal., 4 (1965) 123.
- 34 M. Hansen, 'The Constitution of Binary Alloys', McGraw-Hill, New York, (1958) 631.
- 35 S.A. Golubtsov, V.V. Korobov, K.K. Popkov, I.V. Trofimova, R.A. Turetskaya, K.A. Andrianov, Z.V. Belikova, R.M. Golosova, A.A. Oigenblik and V.G. Aristova, Bull. Acad. Sci. USSR. Div. Chem. Sci., (1966) 965.
- 36 J.R. Anderson and B.H. McConkey, J. Catal., 11 (1968) 54.
- 37 F.A. Veer, B.H. Kolster and W.G. Bergers, Trans. Met. Soc., AIME., 242 (1968) 669.
- 38 S.A. Golubtsov, K.A. Andrianov, R.A. Turetskaya, Z.V. Belikova, I.V. Trofimova and N.G. Morozova, Dokl. Akad. Nauk SSSR., 151 (1963) 656 [English translation].
- 39 R.J.H. Voorhoeve and J.C. Vlugter, J. Catal., 4 (1965) 220.
- 40 L. Brewer and N. Lofgren, J. Am. Chem. Soc., 72 (1950) 3038.
- 41 C.H. Wong and V. Schomaker, J. Phys. Chem., 61 (1957) 358.
- 42 H.M. Rosenstock, J.R. Sites, J.R. Walton and R. Baldock,

- J. Chem. Phys., 23 (1955) 2442.
- 43 W.F. Banholzer, N. Lewis and W. Ward, J. Catal., 101 (1986) 405; and refs. therein.
- 44 J.G. Martin, M.A. Ring and H.E. O'Neal, J. Catal., 102 (1986) 266.
- 45 S.A. Golubtsov, K.A. Andrianov, N.T. Ivanova, R.A. Turetskaya, N.S. Fel'dshtein, E.A. Chernyshev and V.G. Dzvonnar, J. Gen. Chem. USSR., 45 (1975) 795.
- 46 I.M. Podgornyi, S.A. Golubtsov, K.A. Andrianov and E.G. Mangalin, J. Gen. Chem. USSR., 44 (1974) 745.
- 47 I.M. Podgornyi, S.A. Golubtsov, K.A. Andrianov and E.G. Mangalin, J. Gen. Chem. USSR., 44 (1974) 739.
- 48 V.I. Zubkov, M.V. Tikhomirov, K.A. Andrianov and S.A. Golubtsov, Dokl. Akad. Nauk SSSR., 159 (1964) 1221; and refs. therein. [English translation]
- 49 V.I. Zubkov, M.V. Tikhomirov, K.A. Andrianov and S.A. Golubtsov, Dokl. Akad. Nauk SSSR, 188 (1969) 772 [English translation].
- 50 K.A. Andrianov, M.V. Tikhomirov, S.A. Golubtsov, V.I. Zubkov, V.K. Potapov and V.V. Sorokin, Dokl. Akad. Nauk SSSR., 194 (1970) 723 [English translation].
- 51 V.I. Zubkov, S.A. Golubtsov, K.A. Andrianov and M.V. Tikhomirov, Bull. Acad. Sci. USSR. Div. Chem. Sci., (1973) 99.
- 52 L. Holzappel, Z. Elektrochem., 54 (1950) 273.
- 53 W.J. Ward and J.M. Carroll, J. Electrochem. Soc., 129 (1982) 227.
- 54 S.K. Gupta and A.K. Sharma, J. Catal., 93 (1985) 68.
- 55 T.M. Gentle and M.J. Owen, J. Catal., 103 (1987) 232.
- 56 N.P. Lobusevich, L.A. Malysheva, T.D. Novikova, S.A. Golubtsov and L.D. Sporykhina, J. Gen. Chem. USSR., 43 (1973) 947.
- 57 N.P. Lobusevich, N.P. Malysheva, P.A. Pinchuk, M.I. Tsy-pin, L.I. Kleimova, L.P. Sporykhina and V.I. Chickaeva, J. Appl. Chem. USSR., 49 (1976) 2168.
- 58 N.S. Fel'dshtein, A.P. Belyi, A.I. Gorbunov and S.A. Golubtsov, Russ. J. Phys. Chem., 43 (1969) 621.
- 59 N.S. Fel'dshtein, A.I. Gorbunov, A.P. Belyi and S.A.

- Golubtsov, J. Phys. Chem., 45 (1971) 1423.
- 60 N.S. Fel'dshtein, A.I. Gornunov, A.P. Belyi, S.A. Golubtsov and V.T. Sharafanov, Russ. J. Phys. Chem., 43 (1969) 411.
- 61 V. Bažant and J. Joklik, Coll. Czech. Chem. Comm., 38 (1973) 3176.
- 62 V. Bažant and J. Joklik, Coll. Czech. Chem. Comm., 37 (1972) 3772.
- 63 I.M. Podgornyi, A.I. Gorbunov and S.A. Golubtsov, Russ. J. Phys. Chem., 43 (1969) 1501.
- 64 S.A. Golubtsov and I.M. Podgornyi, Russ. J. Phys. Chem., 47 (1973) 1634.
- 65 L.P. Morozova, K.A. Andrianov, N.G. Morozov and S.A. Golubtsov, Bull. Acad. Sci. USSR. Div. Chem. Sci., (1966) 446.
- 66 P.P. Singhalia, G.K. Wattal and D. Kunzru, Chem. Eng. Sci., 38 (1983) 469.
- 67 (a) T.C. Frank and J.L. Falconer, Appl. Surf. Sci., 14 (1982-83) 359.
(b) W.F. Banholzer and M.C. Burrell, Surf. Sci., 176 (1986) 125.
- 68 D. McLeod Jr., K.M. Lewis and B. Kanner, XX-Organosilicon Symposium, Tarrytown, NY., April 1986, p. 1.16
- 69 W.F. Banholzer and M.C. Burrell, J. Catal., 114 (1988) 259.
- 70 K.M. Lewis, D. McLeod and B. Kanner, Catalysis 38 (1987) 415; ed. J.W. Ward, 'Stud. Surf. Sci. Catal.'; and refs. therein.
- 71 J.L. Falconer and J.P. Agarwala, XX-Organosilicon Symposium, Tarrytown, N.Y., April 1986, p. 2.17.
- 72 M.G.R.T. De Cooker, R.P.A. van den Hof and P.J. van den Berg, J. Organomet. Chem., 84 (1975) 305.
- 73 A.I. Gorbunov, A.V. Shchegolev, A.P. Belyi and S.A. Golubtsov, Russ. J. Phys. Chem., 46 (1972) 361.
- 74 I. Shiihara and J. Iyoda, Bull. Chem. Soc. Jpn., 32 (1959) 636.
- 75 K. Terakura, J. Phys. Soc. Jap., 40 (1976) 450.
- 76 A. Hiraki, S. Kim, W. Kammura and M. Iwami, Appl. Phys.

- Lett., 34 (1979) 194.
- 77 (a) A. Cros, F. Salvan, M. Commadre and J. Derrien, Surf. Sci., 103 (1981) L109.
(b) S-H. Chou, A.J. Freeman, S. Grigoras, T.M. Gentle, B. Delley and E. Wimmer, J. Chem. Phys., 89 (1988) 5177
- 78 M.G.R.T. De Cooker, J.W. De Jong and P.J. van den Berg, J. Organomet. Chem., 86 (1975) 175.
- 79 S.A. Golubtsov, K.A. Andrianov, N.T. Ivanova, R.A. Turetskaya, I.M. Podgornyi and N.S. Fel'dshtein, J. Gen. Chem. USSR., 43 (1973) 1985.
- 80 S.A. Golubtsov, K.A. Andrianov, N.T. Ivanova, R.A. Turetskaya and N.S. Fel'dshtein, Bull. Acad. Sci. USSR. Div. Chem. Sci., (1973) 2672.
- 81 R. Müller and H. Gumbel, Z. Anorg. Allg. Chem., 327 (1964) 293.
- 82 K.A. Andrianov, G.I. Belik, N.P. Lobusevich and N.V. Minova, J. Appl. Chem. USSR., 48 (1975) 2117.
- 83 M.G.R.T. De Cooker and P.J. van den Berg, Rec., J. Royal Neth. Chem. Soc., 94 (1975) 305.
- 84 R. Müller and H. Gumbel, Z. Anorg. Allg. Chem., 327 (1964) 302.
- 85 J. Joklik, M. Kraus and V. Bažant, Coll. Czech. Chem. Comm., 27 (1962) 294.
- 86 N.T. Ivanova, L.D. Progozhina, S.A. Golubtsov and A.I. Gorbunov, J. Gen. Chem. USSR., 42 (1972) 1104.
- 87 V.F. Popenko, S.A. Generalova, E.G. Efremov, V.A. Federov, A.S. Malkova, A.S. Pashinkin and N.D. Zverolevleva, J. Appl. Chem. USSR., 55 (1982) 389.
- 88 G.G. Filippov, A.I. Gorbunov, A.P. Belyi and S.A. Golubtsov, Russ. J. Phys. Chem., 46 (1972) 199.
- 89 A.I. Gorbunov, G.G. Filippov and A.P. Belyi, The Sov. Chem. Ind., (1979) 783.
- 90 S.A. Golubtsov, N.T. Ivanova, L.D. Progozhina, K.A. Andrianov, M.A. Ezerets and N.S. Fel'dshtein, Bull. Acad. Sci. USSR. Div. Chem. Sci., (1972) 584.
- 91 P.W. Schenk and H. Bloching, Z. Anorg. Allg. Chem., 334 (1964) 57.
- 92 H. Schäfer and J. Nickl, Z. Anorg. Allg. Chem., 274 (1953)

- 250.
- 93 P. Timms, *Chem. Eng. News*, 45 (1967) 57.
- 94 P.L. Timms, *Inorg. Chem.*, 7 (1968) 387.
- 95 W.H. Atwell and D.R. Weyenberg, *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 469; and refs. therein.
- 96 E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova, *J. Organomet. Chem.*, 271 (1984) 129.
- 97 P.P. Gaspar, *React. Intermed.*, 3 (1985) 333; and refs. therein.
- 98 R.A. Turetskaya, N.T. Ivanova, K.A. Andrianov and E.A. Chernyshev, *J. Gen. Chem. USSR.*, 46 (1976) 1264.
- 99 A.P. Belyi, A.I. Gorbunov, R.M. Flid and S.A. Golubtsov, *Russ. J. Phys. Chem.*, 43 (1969) 637.
- 100 R.A. Turetskaya, N.T. Ivanova, N.S. Fel'dshtein and E.A. Chernyshev, *J. Gen. Chem. USSR.*, 44 (1974) 2738.
- 101 J. Joklik and V. Bažant, *Coll. Czech. Chem. Comm.*, 29 (1964) 603, 834.
- 102 A.I. Gorbunov, K.A. Andrianov, G.G. Filippov, A.P. Belyi, S.A. Golubtsov and N.S. Fel'dshtein, *Dokl. Akad. Nauk SSSR.*, 194 (1970) 626 [English translation].
- 103 A.P. Belyi, A.I. Gorbunov, N.S. Fel'dshtein and S.A. Golubtsov, *Russ. J. Phys. Chem.*, 46 (1972) 303.
- 104 M.G.R.T. De Cooker, J.H.N. Bruyn and P.J. van den Berg, *J. Organomet. Chem.*, 99 (1975) 371.
- 105 G. Sadowski and G. Meier, *Z. Anorg. Allg. Chem.*, 443 (1978) 189.