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New Ideas on the Mechanism of Direct Syntheses of Alkyl(aryl)chlorosilanes

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Studies on the direct syntheses of alkyl(aryl)chlorosilanes, which have served as a basis for the development of new ideas on the reaction mechanism formulated mainly in the last 2-3 years, are reviewed. The direct syntheses are used in the industrial manufacture of the most important organosilicon monomers. The new ideas on the mechanism proved to be extremely useful in determining the rules for the control of technological processes. The ideas concerning the specific role of chlorine transfer processes and the chain mechanism of the formation of alkyl(aryl)chlorosilanes which are discussed here were not dealt with in the previous reviews.
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I. INTRODUCTION

Data on the reaction kinetics and the adsorption of gaseous reactants are examined in detail in the published reviews on the mechanisms of the direct syntheses of alkyl(aryl)-chlorosilanes[1-5], but other extremely important aspects of the reaction mechanism are discussed inadequately, since they began to be considered in the literature only in the last few years. These aspects are the decisive role and mechanism of chlorine transfer from the organic chloride to silicon and also the composition and importance of the surface intermediates.

The ideas developed in the above investigations explained the observed findings and in many cases made it possible to formulate the research needed to intensify and improve the direct syntheses, which constitute the foundation of the industrial manufacture of the principal organosilicon products[6,7].

The direct synthesis of alkyl(aryl)chlorosilanes is an extremely complex and specific heterophase catalytic process in which a multicomponent mixture of compounds is formed and the properties of the solid reactant change significantly in the course of the reaction. For this reason, chemical methods were resorted to (and proved to be fruitful) together with physical and physicochemical procedures. The extensive experimental data accumulated in the development of technological processes also proved to be very useful.

The results of the main studies devoted to the mechanism of the direct syntheses of alkyl(aryl)chlorosilanes are surveyed in the present review in the light of new ideas.

II. SURFACE INTERMEDIATES—PRODUCTS OF THE PARTIAL CHLORINATION OF SILICON

The bonds linking silicon atoms in the crystal lattice are extremely strong (the heat of sublimation of silicon is 110 kcal mole^{-1})[8] and are broken only under the influence of powerful reagents, for example halogens, hydrogen halides, or alkalis. The breakdown of the silicon crystal lattice, which is necessary for the reaction with organic chlorides, also begins in all probability with attack on its surface atoms (primarily those with unsaturated valences, of which there are about 10% according to Haneman[9]) by chlorine. The affinity of silicon for chlorine is illustrated, in particular, by the high strength of the Si–Cl bond (85 kcal mole^{-1} compared with 58 kcal mole^{-1} for the Si–C bond[10]).

In the absence of a catalyst, direct syntheses of alkyl-(aryl)chlorosilanes begin only when chlorine or hydrogen chloride is introduced or at the decomposition temperature of the organic chloride, especially with evolution of hydrogen chloride[11-17]. Therefore a decrease of the decomposition (dehydrochlorination)[18] temperature in the series of alkyl chlorides with increase in the size of the alkyl group is correlated with the decrease of the temperature of the direct synthesis of the corresponding alkylchlorosilanes (the yields of $RSiHCl_2$, $RSiCl_3$, and $HSiCl_3$ are then higher and those of R_2SiCl_2 are lower than in the synthesis of the lowest alkylchlorosilanes[19-22]). The introduction of hydrogen chloride[23-32] or its additional formation in the reaction zone[7,33-35] as a rule accelerates the processes sharply.

Therefore studies dealing with the induction period in the direct syntheses are of considerable interest[36-38]. Investigations by pulse chromatography showed that the induction period is due primarily to the decomposition reactions of the organic chloride; chlorine is then fully bound to the surface of the solid reactant. In the desorption from the solid surface at the end of the induction period at 450 to 600°C, a relatively large amount of trichlorosilane and silicon tetrachloride, which appear to be the main products of the secondary reaction[39], is removed and chlorine and hydrogen chloride are evolved in very small quantities. The formation of alkyl(aryl)chlorosilanes at an appreciable rate begins when a definite amount of bound chlorine is present on the solid surface[38]. Therefore preliminary treatment of the solid reactant by chlorinating agents leads to a decrease of the temperature of the start of the formation of alkyl(aryl)chlorosilanes in the subsequent reaction between the solid and the organic chloride. The removal of chlorination products leads to the deactivation of the solid reactant, while its repeated treatment by chlorine or hydrogen chloride restores its reactivity[37,40].

In a number of studies[11,12,41-51], starting with those of the discoverer of the direct synthesis (Rochow)[11], the involvement of intermediates—products of the partial chlorination of silicon of the type of $SiCl_n$ (where $n < 4$) and HSiCl, was postulated.

Assuming the involvement of organic radicals in the formation of alkyl(aryl)chlorosilanes, Rochow showed that methyl radicals obtained from tetramethyl-lead add to chlorinated silicon only (chloromethylsilanes, which are formed as long as chlorine is present on the surface, were subsequently also detected[52] at 500°C in the reaction of dimethyl ether with a silicon–copper alloy subjected to preliminary treatment with hydrogen chloride). However, this reaction does not occur with $SiCl_4$. On this basis, Rochow proposed a mechanism for the formation of alkyl(aryl)chlorosilanes with participation of partial silicon chlorination products. Similar views on the mechanism of the direct synthesis were expressed by other investigators[45–47]. Czech investigators used the concept of the involvement of the surface compound $SiCl_2$ in devising mechanisms for the formation of $HSiCl_3$ (Joklik and Bažant[43]) and CH_3SiCl_3 (Joklik and Bažant[44]).

The experimental data for the direct syntheses, on which a mechanism of the formation of chloromethylsilanes, chloroethylsilanes, and trichlorosilane with participation of the compounds $SiCl_n$ and HSiCl can be based[12,42,53], were subsequently confirmed by kinetic studies[48–50,54].

There are literature data for the formation of the partial silicon chlorination product $SiCl_2$ by the reaction of silicon tetrachloride with silicon above 1000°C[55–66] and also by the pyrolysis of trichlorosilane, hexachlorodisilane, or perchloropolysilanes[67–69]. The results of kinetic[56], spectroscopic[60], and mass-spectrometric[61] studies on this compound have been published. It has been established that dichlorosilylene can be readily inserted in an M–Cl bond (M = B, P, or C)[70]; when it reacted with methyl chloride in the presence of copper at 350°C, it was possible to obtain chloromethylsilanes[71]. Interesting synthetic possibilities involving the use of dichlorosilylene for the preparation of organosilicon heterocyclic compounds[67,69] and other substances[72] have been demonstrated. The preparation and properties of the chloropolysilanes $(SiCl)_x$,[73] $(SiCl_2)_x$,[71,74], etc.[75–78] have been studied.

In an investigation[79] of the mechanism of the chlorination of metals it was claimed that the addition of chlorine takes place in the gas phase as a result of the reaction with the metal vapour which is always present at the surface. On the other hand, other workers[80] believe that the chlorination of silicon takes place on the surface with participation of atoms linked to one another. It has been stated[41] that the first chlorine atom adds to silicon in the solid phase and the remaining silicon valencies are saturated in the gas phase.

Mass-spectrometric studies on the products of the reaction of silicon with chlorine[81], hydrogen chloride[82], and copper(I) chloride[83] demonstrated the formation on the surface of SiCl, $SiCl_2$, and $SiCl_3$, which can escape into the gas phase under certain conditions[82–84]. The possibility of the existence of gaseous SiCl, $SiCl_2$, and $HSiCl_2$ was confirmed by thermodynamic calculation and the existence of $SiCl_2$ was confirmed by ultraviolet spectroscopic data[85].

The products obtained by the partial chlorination of silicon can react with methyl chloride after being desorbed into the gas phase[42]. However, the gas-phase reactions are apparently unimportant for the direct synthesis: studies on the kinetics and mechanisms of the reactions lead to the conclusion that the formation of hydrogen-containing and alkyl(aryl)chlorosilanes is a purely heterogeneous process[21,86–94]. The application of the method involving separate calorimetric measurements[95–98] showed that all the exothermic stages of the processes take place on the surface. Consequently the main bulk of the products of the partial chlorination of silicon react in the direct synthesis as surface compounds. Recent studies yielded experimental data on their properties, compositions, and role in the overall processes involved in the direct synthesis.

It has been shown that products obtained by the chlorination of the silicon surface are comparatively stable both at room temperature and at the temperatures of the syntheses. It has been established mass-spectrometrically that, even several hours after formation, they can be desorbed from the surface by hydrogen chloride in the form of trichlorosilane close to room temperature[82] or by evacuation at an increased temperature[39]; they can be fully desorbed only after heating the specimens at 600°C for many hours[37] (the claim that the desorption ceases after the specimens of chlorinated silicon have been heated at 310°C[82] is inconsistent with the results of experiments in which the chlorination products were involved in the reactions at temperatures of about 500°C[37,52]).

To determine the nature and compositions of these compounds, formed directly in the reaction zone under the conditions of direct synthesis, the silicon surface containing the partial chlorination products was methylated by methylmagnesium chloride and was rechlorinated after the removal of magnesium chloride; a mixture containing CH_3SiCl_3, $(CH_3)_2SiCl_2$, and $(CH_3)_3SiCl$ was formed[99]. The interaction of chlorinated silicon with the Grignard reagent to form an $Si-CH_3$ group is possible only in the presence of a covalent bond between chlorine and silicon. On this basis, the authors concluded that the chlorination of silicon, which is responsible for the sharp increase of its reactivity in the subsequent reaction with an organic chloride, leads to the formation of the surface intermediates SiCl, $SiCl_2$ and $SiCl_3$ [corresponding to the formation of CH_3SiCl_3, $(CH_3)_2SiCl_2$, and $(CH_3)_2SiCl$].

The presence of the surface compounds $SiCl_n$ alters significantly the state of the surface and its adsorption properties. Adsorption studies by the contact potential difference (CPD) method showed that the chemisorption of the organic chloride from the solid reactant surface in the positively charged β-form is the initial stage of the direct synthesis responsible for the weakening of the bond between silicon (acceptor) and the crystal lattice[100–103]. After treating a silicon–copper alloy (2.4% Cu) with hydrogen chloride at 150°C, the nature of the subsequent chemisorption of hydrogen chloride on the alloy changes appreciably, in particular the positively charged form of the adsorbate becomes more stable[104]. The strengthening of the adsorption linkage between HCl and the silicon–copper alloy (8.63%) after its exposure to an atmosphere of HCl is also indicated by chromatographic data[105].

The presence of Si–Cl bonds on the silicon surface promotes more active chemisorption of methyl chloride on the latter. The desorption of the chlorination product as a result of the heat treatment of the specimen *in vacuo* lowers its adsorption capacity, which is reduced to a minimum after heating at 1150°C; the synthesis of chloromethylsilanes directly afterwards promotes the restoration of the adsorption capacity of the specimen[46]. To a first approximation, the adsorption of methyl chloride on the chlorinated specimen in the β-form active in the direct synthesis corresponds to a change in the surface potential, which is approximately twice as large as in adsorption on the nonchlorinated specimen[106].

Some authors[106–108] believe that the compounds $SiCl_n$ are responsible for the formation of active centres on which the reacting organic chloride molecule is adsorbed: its interaction with silicon is facilitated by the presence of an electronegative substituent at the silicon atom in the crystal lattice. It has been shown[107] that, when silicon is treated with hydrogen fluoride rather than hydrogen chloride, the

temperature of the start of its reactions with methyl chloride is reduced even more: the higher electronegativity of fluorine present as a substituent at the silicon atom facilitates to a greater extent the interaction of the halogenated silicon with methyl chloride. One of the causes of this is the stronger bond between the chlorine atoms of the adsorbed organic chloride molecules and the halogenated silicon atoms on the surface compared with the non-halogenated atoms. Bonds involving *d* orbitals (in particular chemisorption bonds) are known to be strengthened when electronegative substituents are attached to silicon[109] (in our case chlorine). The strengthening of the adsorption linkage between the organic chloride and silicon weakens the bonds between the silicon atom and the crystal lattice and is a necessary condition for the rupture of these bonds[106].

In the latest systematic studies on the kinetics and mechanisms of the reactions of HX[4,5,48,104,110–112] and CH_3X[4,5,111] (X = Cl or Br) with silicon and germanium the idea that the M–M bond strength (where M = Si or Ge) determines the rate of the direct synthesis of hydrogen-containing silanes and germanes, halogenomethylsilanes, and halogenomethylgermanes has been developed. In support of these views, the authors quote in the first place the following evidence: (1) the decrease of the reaction temperature and activation energy with increase in the amount of impurities in silicon facilitating the dissociation of the Si–Si bonds in the transition state[48,104,113]; (2) the increase of the plasticity of the surface layers of single-crystal silicon due to the decrease of the specific surface energy of the crystal and hence of the Si–Si bond strength as a result of the introduction of microamounts of copper (0.0013–0.3%), which tend to increase the reactivity of silicon in the synthesis of trichlorosilane and dichloromethylsilane[111]; (3) the similarity of the kinetic characteristics of the reactions of silicon or germanium with HX or CH_3X regardless of the nature of the halogen (chlorine or bromine)[4,5,110]; (4) the correlation between the Si–Si and Ge–Ge bond strength on the one hand and the activation energy of the chlorination of hydrobromination of silicon and germanium on the other [112]; (5) the parallel variation of the activation energies for the synthesis of trichlorosilane or trichlorogermane with M–M bond strengths following the introduction of germanium into silicon or conversely[5]. All these findings are satisfactorily consistant with the postulated involvement of surface compounds containing Si–Cl bonds, which weaken the bonds between silicon atoms and the crystal lattice, in the formation of active centres.

These ideas are also confirmed by results[100,103] obtained in studies of the chemisorption of various chloro-derivatives on solid reactants treated with hydrogen chloride at 450°C, i.e. containing the surface products of the partial chlorination and hydrochlorination of silicon, although the authors assume without experimental evidence that the chemisorption takes place at silicon atoms.

Surface compounds of the type SiX_n are directly involved in the formation of the final products of the direct synthesis. This has been confirmed experimentally[99,107]. In the reaction of methyl chloride with the surface of silicon treated with hydrogen fluoride, the products are fluoromethylsilanes and chorofluromethylsilanes[99]. An increase in the degree of preliminary chlorination of silicon leads to an increase of the amount of chloromethylsilanes obtained in the reaction between silicon and methyl chloride injected in a single pulse under conditions which virtually rule out the supplementary formation of the compounds $SiCl_n$.[107]

The products of the partial chlorination of silicon on the surface also serve as active centres for the decomposition of the organic chloride. For example, in the interaction of methyl chloride with chlorinated silicon, even under the conditions of a very low degree of chlorination where chloromethylsilanes still cannot be detected, the amount of hydrocarbons is significantly greater than in the reaction with non-chlorinated silicon[107].

Ideas concerning the composition of the products of the partial chlorination of silicon and the mechanism of their involvement in the formation of alkyl(aryl) chlorosilanes (with and without catalysts), which follow from experimental results, were first put forward in a study of the synthesis of chlorophenylsilanes (for R_2SiCl_2 and $RSiCl_3$)[108,114] and chloroethylsilanes (for $RSiHCl_2$ and partly $RSiCl_3$)[12].

Subsequently the identification of fluoromethylsilanes and chlorofluoromethylsilanes, obtained in the reaction of methyl chloride with solid reactant surfaces subjected to a preliminary treatment with hydrogen fluoride, confirmed the above hypothesis[99]. The possibility of the involvement of SiX, SiX_2, and SiX_3 in the formation of $RSiX_3$ and of SiX in the formation of R_2SiX_2 was demonstrated; the formation of $RSiHX_2$ with participation of HSiX cannot be ruled out. CH_3SiFCl_2, CH_3SiF_2Cl, CH_3SiF_3, and $(CH_3)_2SiFCl$ were clearly identified and $CH_3SiHFCl$ and $(CH_3)_3SiF_2$ were tentatively identified in the reaction of methyl chloride with surface compounds of the type SiF_n. Additional data for the compositions of the intermediates in the direct synthesis were obtained in a study of the interaction between dimethyl ether and the surfaces of solid reactants treated with Cl_2 or HCl.[115] The compound $HSiCl_2$ (corresponding to CH_3SiHCl_2 detected in the products), which is probably involved in the formation of $RSiHCl_2$, can exist on the surface together with SiCl, $SiCl_2$, $SiCl_3$, and HSiCl. In another investigation the silicon surface was treated with hydrogen chloride or chlorine under the conditions of the preferential formation of products of the partial chlorination of silicon on the surface: SiCl or $SiCl_2$ and $SiCl_3$. $(CH_3)_2SiCl_2$ or CH_3SiCl_3 respectively predominated in the products of the reaction of methyl chloride with the surface of the chlorinated silicon specimens[107].

Since different final products can be formed (depending on the properties of the solid reactant and the reaction conditions) in reactions involving the same surface compound (see p.15), a clear correlation between the composition of the compounds $SiCl_n$ and the final reaction products is on the whole impossible. Thus, under the conditions of rapid decomposition of organic chlorides, the compounds SiCl are gradually converted into $SiCl_3$, participating ultimately in the formation of $RSiCl_3$. The same applies to the compounds $SiCl_2$. If the rate of decomposition is low and the reactivity of the solid with respect to the formation of the Si–C bond is adequate (mainly in the presence of a catalyst), the compounds SiCl are probably involved mainly in the formation of R_2SiCl_2 and the compounds $SiCl_2$ are involved in the formation of alkyl(aryl)trichlorosilanes[99,108].

III. THE MECHANISM OF CHLORINE TRANSFER FROM THE ORGANIC CHLORIDE TO SILICON

1. The Transfer of Chlorine in the Formation of Individual Alkyl(aryl)chlorosilanes.

A seemingly paradoxical increase not only of the overall reactivity but also of the selective reactivity of the solid reactants in the formation of dialkyl(aryl)chlorosilanes (compounds with a relatively low chlorine content) after the introduction into the reaction of small amounts of chlorine or chlorine donors (HCl, CuCl, $HSiCl_3$, etc.) has been observed

in studies on the synthesis of chloromethylsilanes[7], chloroethylsilanes[53], and chlorophenylsilanes[106,114,116,117]. For example, the addition of 0.5–1.5% CuCl increases the yield of dichlorodiethylsilane by 25–30%[53,85] and the addition of water, which leads to the formation of hydrogen chloride in the reaction zone, increases the yield by a factor of 1.5.[53] Fig. 1 illustrates the influence of added hydrogen chloride on the reaction of chlorobenzene with a solid reactant consisting of a mixture of silicon and copper powders (40%)[108]. With increase of hydrogen chloride concentration in the reaction mixture to 12%, the rate of formation of dichlorodiphenylsilane increases approximately by a factor of five, despite the fact that hydrogen chloride is not involved in the overall reaction whereby it is synthesised.

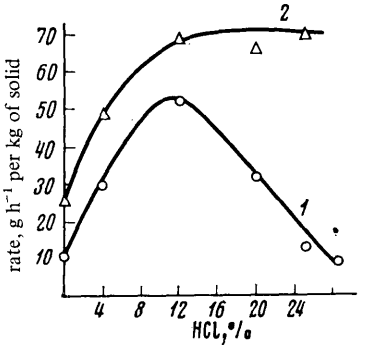


Figure 1. Variation of the rates of formation of dichlorophenylsilane (curve *1*) and trichlorophenylsilane (curve *2*) as a result of the introduction of hydrogen chloride in the synthesis of the chlorophenylsilanes on a mixture of silicon and copper powders.

In the direct synthesis of trichlorophenylsilane without a catalyst (at about 600°C with the ratio HCl : C_6H_5Cl = 1 or 4–1.8)[7,15], hydrogen chloride is again not involved in the overall reaction scheme, in contrast to other processes for the synthesis of alkyl(aryl)trichlorosilanes[37,118]: the yield of trichlorophenylsilane is about one mole for three moles of the chlorobenzene which has reacted and the overall amount of silicon tetrachloride and trichlorosilane corresponds to the amount of hydrogen chloride which has reacted. In the absence of hydrogen chloride, the reaction barely proceeds (the degree of conversion of chlorobenzene does not exceed 5%).

Such experimental results suggested that chlorine or chlorine donors, in particular CuCl and HCl which react with silicon to form the surface compounds $SiCl_n$, initiate the process, the compounds $SiCl_n$, which serve as the active centres for the reaction, being regenerated[106,108]. Similar ideas about the mechanism of the formation of dialkyldichlorosilanes were put forward in early investigations[53,85], where it was found that the amount of chlorine in dichlorodiethylsilane, formed when ethyl chloride interacts with chlorinated silicon in the absence of a catalyst, greatly exceeds the amount of chlorine combined in the preliminary chlorination of silicon.

The employment of pulse chromatography yielded an experimental confirmation of these ideas about the direct syntheses[99,107].

Silicon tetrachloride and chloromethylsilanes were detected together with chlorofluoromethylsilanes when silicon treated with hydrogen fluoride was allowed to react with methyl chloride at 350–450°C. The interaction of methyl chloride with non-halogenated silicon atoms is virtually ruled out under these conditions. Therefore the formation of halogeno-derivatives of silicon without fluorine might have been a consequence only of the addition of chlorine to silicon atoms adjoining the SiF_n surface species, i.e. a consequence of the regeneration of the surface compound — a product of the partial chlorination of the adjoining silicon atom after the completion of the cycle involving the formation of alkyl(aryl)chlorosilanes[99].

The deactivation of the solid reactants after the desorption of $SiCl_n$ and the restoration of their reactivity on chlorination show that constant regeneration of these compounds during synthesis is a necessary condition for the retention of the reactivity of the solid reactant in the course of the entire process[106].

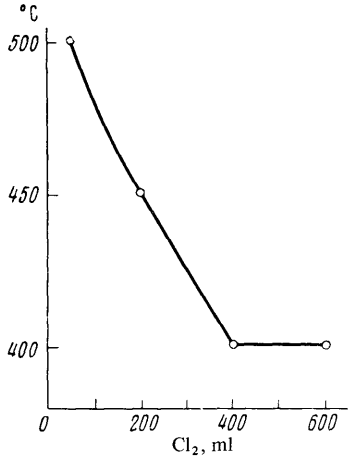


Figure 2. Effect of the degree of chlorination of silicon on the measured temperature of its steady reaction with methyl chloride.

It is very significant that preliminary chlorination of silicon lowers not only the temperature of the beginning of its reaction with methyl chloride but also the temperature of the development of the process in which the rate of the reaction already begun does not decrease during subsequent injections of methyl chloride. An increase in the degree of chlorination lowers the observed temperature of the steady reaction involving the formation of chloromethylsilanes (Fig. 2)†. Since a steady reaction requires that the products of the partial chlorination of silicon be replenished and

† The gradual inhibition of the formation of trichloromethylsilane and $SiCl_4$ as $SiCl_n$ is removed, observed[37] in the reaction of methyl chloride with the surface of chlorinated silicon at 350–500°C, is associated with the fact that the chlorination was carried out with 200 ml of chlorine at 350°C; Fig. 2 presents the results of experiments with specimens chlorinated at 400°C.[107]

at the temperatures considered (below 600°C) the decomposition of methyl chloride on silicon with formation of $SiCl_n$ is negligible, evidently $SiCl_n$ is renewed in the course of the reaction itself[107]. Only the decomposition of RCl [without the formation of alkyl(aryl)chlorosilanes] on the active centres leads to the ultimate formation of chlorosilanes alone and is not accompanied by the generation of new active centres.

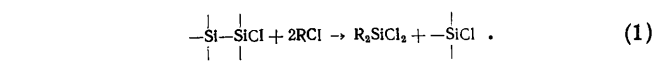
Semenov, Voevodskii, and Vol'kenshtein[119–121], Roginskii[122], and others[123] developed hypotheses concerning heterogeneous-catalytic processes with surface or fixed chains, occurring on repetition of reaction cycles at the active centres formed previously on the catalyst surface. Such views are close to those concerning the catalytic process involving a non-stoichiometric initiator, for example carbon monoxide, in the hydropolymerisation of olefins on a cobalt catalyst[124–126]. Polymerisation, initiated hydropolymerisation, and the synthesis of hydrocarbons from CO and H_2 are nowadays classified as catalytic processes involving the formation of surface chains[127].

The study of the mechanism of the direct synthesis of alkyl(aryl)chlorosilanes suggests that many reactions involved in this process, which are of greatest practical importance, can be classified as catalytic heterophase reactions with surface chains proceeding with participation of an initiator[99,106–108,114]. The initiators can be chlorine or chlorine donors (CuCl and HCl). They form surface compounds of the type $SiCl_n$ (by partial chlorination of silicon), which are involved in the formation of active centres for the reaction. The chemisorption and subsequent reaction of the organic chloride at the active centres lead to the formation of the final reaction products with regeneration of the active centre at an adjoining silicon atom. The cycle is completed by the desorption of the final product into space and the regeneration of $SiCl_n$ is accompanied by the liberation of other silicon atoms, whose valencies probably remain free and which are thus available for the surface reaction. The characteristic features of the direct synthesis are the formation of initiators (chlorine compounds) in the reaction zone on decomposition of the organic chloride and also the possibility of the occurrence of reactions with participation of initiators introduced from outside.

The data concerning the chain mechanism of the direct synthesis are consistant with the theoretical postulates concerning the chain mechanisms of reactions on the surface of solids. However, an unambiguous confirmation of this requires certain additional quantitative studies, which are of fundamental interest for the solution of general problems of the theory of heterophase reactions of this kind.

Experimental studies on adsorption in direct syntheses of chlorosilanes and alkyl(aryl)chlorosilanes proved the validity of the mechanism involving the chemisorption of the organic chloride without dissociation of a single-atom active centre[103,128]; it has been shown[128] that the hypothesis of the dissociative adsorption of methyl chloride at two centres in the formation of dichlorodimethylsilane[1,21,86–88,93,129] is invalid. In the light of the foregoing one must assume that the active centre on the surface of the solid reactant in the direct synthesis includes silicon atoms, one (for R_2SiCl_2) or more (for $RSiCl_3$) valencies of which are bound to chlorine.

In all probability the reactions in the formation of dialkyl(aryl)chlorosilanes are accompanied by a rearrangement of the coordination sphere with transition of the reacting silicon atom to a state with an increased valence[106,130]. However, we believe that the available data are inadequate to infer unambiguously the composition of the intermediate complexes in the direct synthesis of alkyl(aryl)chlorosilanes. The mechanism of the formation of dialkyl(aryl)chlorosilanes, supported by experimental evidence, can be represented schematically as follows[99,106–108,114]:



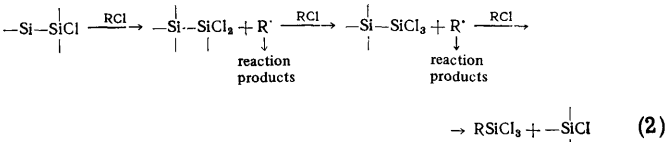
$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{SiCl}} + 2RCl \rightarrow R_2SiCl_2 + -\overset{|}{Si}Cl \quad (1)$$

A similar mechanism was put forward in another study[130], where an attempt was made to elaborate it in greater detail in conjunction with the consideration of tentative intermediate stages, in particular the formation of the surface compounds $RSiCl_2$, etc. The approximate calculations carried out in that investigation confirmed that the formation of the dialkyl(aryl)chlorosilane molecule can be accompanied by the regeneration of the surface compound — the product of the partial chlorination of the silicon atom at the centre of a neighbouring tetrahedron.

The proposed mechanism reflects satisfactorily the experimental findings. The increased yields of dialkyl(aryl)chlorosilanes after the introduction into the reaction of optimum amounts of chlorine donors (HCl and CuCl), the acceleration of the formation of dialkyl(aryl)chlorosilanes in the initial stage of the reaction[131] after the generation of sufficient active centres, and the selective formation of R_2SiCl_2 under conditions where the decomposition processes take place at the minimum rate[7] (the increase of the degree of chlorination of silicon and chain termination in the formation of R_2SiCl_2 are relatively inhibited) can be understood.

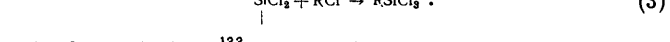
The formation of R_2SiCl_2 at advanced stages in the reaction involving silicon (i.e. as the solid reactant is deactivated) is known to be promoted by a gradual increase of temperature in the reaction zone[132]. The decomposition of the organic chloride is then accelerated. Under certain conditions, this leads to the formation of new active centres, the generation of new chains, and the restoration of the rate of formation of the dialkyl(aryl)chlorosilane.

It has been suggested[107,108] that the formation of alkyl(aryl)trichlorosilanes proceeds in all probability with chain propagation (in the absence of a catalyst):



$$-\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{SiCl}} \xrightarrow{RCl} -\overset{|}{\underset{|}{Si}}-\overset{|}{\underset{|}{SiCl_2}} + R\cdot \xrightarrow{RCl} -\overset{|}{Si}-SiCl_3 + R\cdot \xrightarrow{RCl} \rightarrow RSiCl_3 + -\overset{|}{Si}Cl \quad (2)$$

or with chain termination (in a catalytic process).



$$\overset{|}{SiCl_2} + RCl \rightarrow RSiCl_3 . \quad (3)$$

Podgornyi et al.[133] adopted these mechanisms with an additional consideration of possible intermediate stages.

CH_3SiFCl_2, CH_3SiF_2Cl, and CH_3SiF_3 were evidently detected owing to these factors in the formation of trihalogenomethylsilanes by the reaction of methyl chloride with the surface of silicon treated with hydrogen fluoride[99]. Therefore in the synthesis of trichlorophenylsilane in the absence of a catalyst the introduction of hydrogen chloride (the reaction initiator) makes it possible to increase very sharply (by a factor greater than 10) the rate of formation of the required product[108]. The reaction begins with the interaction of hydrogen chloride involving the formation of $SiCl_n$ active centres. The latter can react with hydrogen chloride, forming trichlorosilane and silicon tetrachloride (their content in the mixture of products is usually about 35%) or the compounds $SiCl_n$ can enter into the composition of the active centres on which chlorobenzene decomposes with formation of more highly chlorinated products and adds

on with regeneration of the products of the partial chlorination of silicon. Thus the amount of consumed HCl corresponds to the amount of trichlorosilane and silicon tetrachloride formed.

In the presence of a catalyst the temperature of the synthesis of chlorophenylsilanes can be reduced by approximately 150 deg C. Then in the absence of hydrogen chloride the formation of the primary active centres involving the surface compounds $SiCl_n$ proceeds mainly in the catalytic decomposition of chlorobenzene and chlorination of silicon by the CuCl formed, which plays the role of an initiator. The additional introduction of relatively small amounts of hydrogen chloride results in this case too in an increase of the rate of the process and (to the greatest extent) of the rate of synthesis of dichlorodiphenylsilane (Fig. 1). With increase of the concentration of hydrogen chloride, the rate of formation and content of dichlorodiphenylsilane in the mixture of reaction products through a maximum. Under the conditions adopted, hydrogen chloride not only initiates the process but also behaves as a reactant in the formation of trichlorophenylsilane, which is illustrated by the sharp decrease of the fraction of products derived from phenyl radicals per mole of trichlorophenylsilane with increase of the amount of added hydrogen chloride[108]. The involvement of hydrogen chloride leads to an increase of the degree of chlorination of the surface compounds and evidently to chain termination. As a result, the overall rate of formation of chlorophenylsilanes falls (with increase of the fraction of trichlorophenylsilane in the reaction products).

When the reaction is carried out in the presence of solid reactants with a high catalytic activity, the overall rate of formation of chlorophenylsilanes in specific syntheses of dichlorophenylsilane is always higher, owing to the chain mechanism of its formation, than in processes with preferential formation of trichlorophenylsilane[20,108,134].

Alkyl(aryl)dichlorosilanes are always formed with participation of hydrogen chloride and the surface intermediates $HSiCl$.[7,53,99,128,135]. The experimental evidence for the mechanism of the process

$$-\underset{\underset{Cl}{|}}{\overset{H}{\overset{|}{Si}}}- \xrightarrow{RCl} RSiHCl_2 \qquad (4)$$

is quite reliable. However, we believe that there is no justification for the total exclusion of chain reactions from this process (for example, with participation of the surface compounds $HSiCl_2$)[115].

The formation of trialkyl(aryl)chlorosilanes R_3SiCl, the products of the disproportionation of alkylation of R_2SiCl_2,[136,137] also involves the chlorination of silicon, which is responsible for the primary formation of R_2SiCl_2.

It is noteworthy that the above mechanisms of the interaction between the organic chloride and the solid reactant is simplified (in particular the role of the copper catalyst in the mechanisms is not taken into account) and do not reflect fully the complex process in which the formation of particular products of the partial chlorination of silicon and the nature of their subsequent interaction with the organic chloride (the intermediates can also interact) are influenced by a multiplicity of different factors.

2. The Role of the Catalyst. The Involvement of Copper in the Transfer of Chlorine from the Organic Chloride to Silicon

With increase of the R–Cl bond strength[138] in the series $C_3H_7Cl < C_2H_5Cl < CH_3Cl < CH_2 = CHCl < C_6H_5Cl$, the temperature of the direct synthesis of the corresponding alkyl(aryl)chlorosilanes rises[7,21,22]. This suggests that the activation of the organic chloride[7,53,85,106] is an important condition for the successful occurrence of the process. Copper is known to catalyse the reactions with organic chlorides[139] and has been used widely[140] also in direct syntheses.

The vast majority of the relevant publications deal with the methods of preparation and properties of the copper catalyst. In considering the role of copper in the direct synthesis of alkyl(aryl)chlorosilanes attention has been concentrated on the activation of silicon.

The activation of pure silicon is possible as a result of the change in the electronic state of the surface atoms ("the collective electronic effect") and the decrease of the Si–Si bond strength when microamounts of copper (about 10^{17} atoms cm^{-3}) are dissolved in it[111,128]. (Shiihara and Iyoda[141] was the first to draw attention to the dependence of the increase of the activity of silicon on the decrease of the Si–Si bond strength when copper, iron, aluminium, or calcium are present in its silicon lattice). However, this effect is characteristic not only of copper but also of certain other elements present in silicon[128,142]. This conclusion is confirmed by the higher reactivity of technical silicon, which usually contains about 2% of impurities, compared with pure silicon in all the direct synthesis investigated[31,48,86,104,113,143]. Therefore the practical importance of this effect of copper in the employment of technical silicon is small and copper does not stabilise the reactivity of various technical silicon specimens differing in their collective electronic properties in the initial state[128].

The increase of the reactivity of surface silicon atoms is more significant when chlorine atoms combine with them[37,106,130]. Surface compounds of the type $SiCl_n$ also behave as centres for the activation of the organic chloride[107].

The involvement of copper in the transfer of chlorine from the organic chloride to silicon via the mechanism

$$RCl + Cu \rightarrow CuCl + R^{\cdot} \text{ or its reaction products,} \qquad (5)$$

$$CuCl + Si \rightarrow -\underset{|}{\overset{|}{Si}}Cl + Cu \qquad (6)$$

was suggested in the first study of the mechanism of the direct synthesis of alkyl(aryl)chlorosilanes[11]. Many investigators who studied the direct synthesis subsequently reached the same conclusion[7,41,45–47,53,141]. Furthermore, it has been shown for the reaction with methyl chloride that the ability of copper to form copper(I) chloride determines to a large extent its activity in the direct synthesis of chloromethylsilanes[144]. An attempt has actually been made[45] to relate the decrease of the induction period in this process to the catalytic influence of the aluminium present in silicon on the formation of CuCl.

Assuming that the stage involving the transfer of chlorine to silicon with participation of CuCl is the most important link in the entire process, Japanese[141,145–150] and German[45–47,151–153] investigators made a detailed study of the reaction between copper(I) chloride and silicon. The temperatures of the onset of reaction[146,151,152] and many other kinetic characteristics[145,147–149] were determined and the different stages of the interaction[148,149,152]; the composition of the compounds formed[152], and the effect of various factors on the reaction[45,141,148–150] were studied.

Interesting data on the involvement of copper in chlorine transfer to silicon with formation of the $SiCl_n$ intermediates were obtained recently in a study of the direct synthesis by pulse gas chromatography[99,107]. When silicon was treated with chlorine, the main product of its subsequent reaction with methyl chloride was trichloromethylsilane[107].

The presence of copper in the silicon alloy was responsible for the formation of dichlorodimethylsilane in similar experiments[99]. Dichlorodimethylsilane was found to predominate also in the reaction of methyl chloride with silicon (in the absence of copper) treated with hydrogen chloride.

Under the conditions adopted, chloromethylsilanes are obtained almost wholly with participation of the $SiCl_n$ surface compounds formed beforehand. When chlorine is replaced by hydrogen chloride in the preliminary treatment of silicon, the species SiCl,[107] whose involvement in the reaction with methyl chloride leads to the formation of dialkyl(aryl)chlorosilanes as the main product, predominates among the $SiCl_n$ surface species instead of $SiCl_2$ and $SiCl_3$. The formation of dichlorodimethylsilane in the reaction with the silicon–copper alloy suggests that in the presence of copper the chlorination of silicon also leads to the preferential formation of SiCl. Thus copper involved in the chlorine transfer processes apparently influences the composition of the compounds $SiCl_n$, promoting the formation of the partial silicon chlorination products which are responsible for the synthesis of dialkyl(aryl)dichlorosilanes.

Therefore the introduction of copper(I) chloride into the reaction zone can increase significantly the content of dialkyldichlorosilanes in the mixture of products. The removal of CuCl from the solid reactant in the direct synthesis (by reducing it with hydrogen) leads to the disappearance of the dialkyldichlorosilane $[(C_2H_5)_2SiCl_2]$ from the reaction products[53,85]. The involvement of the copper catalyst in the transfer of chlorine to silicon probably constitutes an extremely important function of the catalyst in direct syntheses whose temperature is much lower than the temperature of the reaction between copper(I) chloride and silicon.

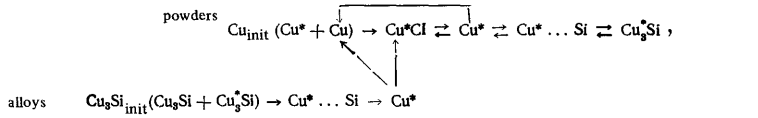
If the decomposition (dehydrochlorination) of the alkyl chloride proceeds at a temperature lower than that at which copper(I) chloride is reduced by silicon or the synthesis is carried out with introduction of hydrogen chloride from outside, the surface products of the partial chlorination of silicon are formed readily also without the involvement of copper (by the reaction between silicon and HCl) and the above function of the catalyst is not manifested. These data have been interpreted in some studies[21,104,111–113,128] as evidence for the rejection of the involvement of CuCl in all the processes of the direct synthesis.

Some investigators refer to the possibility of the synthesis, for example of chloroisopropylsilanes (in which the compounds $SiCl_n$ and HSiCl are formed by the reaction of silicon with hydrogen chloride, produced by the dehydrochlorination of isopropyl chloride) at 110–120°C, while CuCl is reduced by silicon under analogous conditions only at 260°C.[21] Others motivate their objections by the fact that the CuCl introduced from outside did not accelerate the reaction with hydrogen chloride in their experiments[104]. However, under these conditions an acceleration of the reaction was not in fact to be expected, since the synthesis occurred, according to the data of the above investigators themselves, at temperatures (230° and 220°C for the purified and technical silicon respectively[104]) lower than that of the reaction of CuCl with silicon (269° and 234°C for the same silicon specimens[113]). This applies also to the introduction of copper(I) bromide (the temperature of its reduction by silicon is 300°C[112]) in the reaction between hydrogen bromide and silicon (reaction temperature 220°C[110]).

When pure silicon (99.9999%) is used, the temperature of the synthesis of trichlorosilane and dichloromethylsilane (from methyl chloride and hydrogen chloride) increases to 320°C.[104,111]. Therefore it is quite understandable why in the presence of CuCl these products are formed at a temperature as low as 260–280°C,[111] which corresponds according to the author's data, to the temperature of the reduction of CuCl by pure silicon (279°C)[113].

In the synthesis of alkyl(aryl)chlorosilanes (R = CH_3, C_2H_5, or C_6H_5) the introduction of CuCl as a rule activates the reactions[7,53,116] and CuCl is directly involved in the formation of the required product[53,85]. However, the role of CuCl in the direct synthesis of alkyl(aryl)chlorosilanes is apparently not limited to the transfer of chlorine from the organic chloride to silicon. The prolonged activity of the copper catalyst observed in the processes can be accounted for by the high catalytic activity of the copper itself, which is continually formed as a result of the reduction of copper(I) chloride[116]. The activity of the copper catalyst obtained by the reduction of CuCl by silicon has been demonstrated in the synthesis of chloromethylsilanes[21,154]. In particular, at a temperature as low as 250–300°C this copper forms with silicon the intermetallic compound Cu_3Si, while in the presence of crystalline copper, which is relatively inactive in the synthesis, Cu_3Si is obtained only at temperatures above 1000°C.[144]

Generallising from the literature data, the involvement of copper in the synthesis can be represented by a series of complex reversible phase transformations which the most active fraction of the initial copper or Cu_3Si gives rise to CuCl, which is reduced by silicon with formation of unstable catalytically active copper, the intermediate Si–Cu compounds, and ultimately intermetallic phases, including Cu_3Si:[116,117,131]



where an asterisk denotes an active form of copper and Cu is crystalline copper with a low activity.

The activity and the necessary concentration of the initial copper in the reaction zone depend markedly on its properties (for example, the proportion of structural defects) and the conditions in the formation of CuCl [in particular the energetics of reaction (5)][117]. An increased proportion of structural defects can be achieved by mechanical treatment of the powders (copper flakes) or by rapid cooling of silicon–copper alloys[155]. Reaction (5) becomes more favourable on energy grounds, particularly after the addition of promoting additives–Group II elements (see subsection 3 of the present Section).

All this promotes a sharp increase of activity and at the same time a decrease of the optimum catalyst concentration[6]. Possibly not all the copper in the reaction zone catalyses the direct synthesis: the active form of copper is responsible for catalysis. If the entire copper introduced were involved in the process, then in the course of the phase transformation the reactivity of the solid reactants having the same chemical composition would ultimately reach the same level, which is inconsistent with experimental data. Experiment shows that, in order to attain satisfactory rates the selectivities in the synthesis of alkyl(aryl)chlorosilanes in the presence of highly active copper, a very low content of the latter in the solid reactant is sufficient[53,156]. However, under inductrial conditions it is as a rule necessary to employ higher copper concentrations, since during the process part of the copper may be deactivated by harmful impurities in the reactants and by side products and can also undergo recrystallisation[53,157,158]. Therefore, in order to utilise the silicon as fully as possible, it is frequently desirable to introduce the required amount of catalyst gradually in the course of the synthesis and not all at once. This makes it possible to reduce the rates of the

undesirable decomposition reactions of the organic chloride under the influence of the organic chloride under the influence of the excess amounts of copper.

The weakening and dissociation of the C–Cl bond and the formation of CuCl apparently constitute a slower stage than the transfer of chlorine from copper to silicon[116]. Therefore in the direct synthesis of alkylchlorosilanes (280 to 370°C) the steady-state concentrations of copper(I) chloride determined in the solid reactant under experimental conditions are much higher (up to 8%)[85] than in the synthesis of chlorophenylsilanes (at most about 1%)[131], where the formation of CuCl is hindered by the increased strength of the bond between chlorine and the phenyl group[138], the interaction of chlorine with silicon being accelerated at a high temperature in the reaction zone (450°C)[159,160].

Possibly the intermediate CuCl determined in the solid reactants removed from the reactor during the direct synthesis does not constitute an independent phase, but is bound chemically to the solid reactant in the form of a surface compound[21,46]. It is also likely that the product of the reaction of the organic chloride with copper in the solid reactant is more reactive than ordinary CuCl and reacts with silicon at a lower temperature, particularly since ordinary CuCl exists in a polymeric form[161–163].

The composition of the admixtures in silicon greatly influences its reactivity (the temperature of the onset of reaction) in the interaction with CuCl[113,141] and the composition of the compounds formed from CuCl and silicon or from HCl and silicon in the presence of copper[141]. The influence of various elements in the solid reactants on the direct synthesis of chloromethylsilanes[164–169], chloroethylsilanes[143], and chlorophenylsilanes[170], which is known and has been frequently discussed, is in many respects determined by their influence on the formation of surface compounds of the type $SiCl_n$ (in particular from CuCl and silicon), which play a most important role throughout the process.

Intermetallic compounds of copper and silicon, including Cu_3Si (the so called η-phase) evidently serve as a source of the formation and renewal of the catalytically active copper, but it has been established[171] that Cu_3Si does not play the exceptional role which was attributed to it in some investigations[1,21,86,93,129,154,172]. (The activity of the intermetallic phases obtained in the reduction of CuCl by silicon is higher than that of the alloy phases[131,144]).

The intermediate surface compounds of silicon and copper, in the silicon atoms of which electronic changes associated with the local effect of copper (the "local electronic effect") take place, are apparently important for the catalysis of the synthesis of alkyl(aryl)chlorosilanes (without the involvement of hydrogen chloride), in particular of the selective formation of dialkyl(aryl)dichlorosilanes[128]. However, the author does not explain in what way the local effect of copper facilitates the formation of dialkyl(aryl)dichlorosilanes.

3. The Involvement of Promoting Agents in the Transfer of Chlorine from the Organic Chloride to Copper and Silicon.

Analysis of the literature shows that the introduction of promoting additives is the most effective means of increasing the overall activity and of controlling the selectivity of the solid reactants in the direct synthesis. Elements of all the Groups in the Periodic System (and combinations of compounds of these elements), other than those of Groups VI and VII, have been recommended in numerous publications[143,165,166,173–186].

The majority of promoting agents have been discovered empirically and they influence one of the parameters of one or two similar processes. Thus antimony and bismuth activate the synthesis of chloromethylsilanes[31,181] and chloroethylsilanes[53], but do not affect the formation of chlorophenylsilanes[170], while sodium compounds added in the preparation of chloromethylsilanes[179] deactivate the solid reactants in the synthesis of chlorophenylsilanes[170]. Calcium and its compounds promote the preferential formation of hydrogen-containing dichloroethylsilane[143], associated with the dehydrochlorination of ethyl chloride[135], while in the synthesis of chlorophenylsilanes they increase the yield of chlorotriphenylsilanes[170], which is formed without the involvement of hydrogen chloride.

The attempts to explain the mechanism of the effect of certain additives to silicon–copper alloys in the synthesis of chloromethylsilanes[169,187] were not continued, since the proposed explanations are difficult to reconcile with the hypotheses concerning the mechanism of the direct synthesis.

Some investigators[116,117,188] put forward the idea that very effective promoting agents for various direct syntheses, particularly those involving the selective formation of dialkyl(aryl)dichlorosilanes (zinc, cadmium, and their compounds), participate in the transfer of chlorine from the organic chloride to copper and silicon via reactions (5) and (6). The experimental data are in good agreement with this hypothesis.

In the synthesis of chlorophenylsilanes in the presence of the most active promoting agents (cadmium compounds) the solid reactants contain as a rule not less than 1% CuCl, the solid reactants with less active promoting agents (zinc compounds) contain about 0.5% CuCl, while in the absence of promoting agents the CuCl content does not exceed the error of its determination (± 0.05%)[131].

The involvement of CuCl in the phase transformations of the solid reactant is accompanied by the formation of Cu_3Si (Krylov et al.[144]) (see also the scheme on p. 218. Therefore the relative content of Cu_3Si in the solid reactant can serve by convention as a measure of the involvement of CuCl in the process. When a mixture of silicon and copper powders is heated in the presence of promoting agents ($ZnCl_2$, $CdCl_2$) in an atmosphere of nitrogen at 450°C, the intermetallic compound Cu_3Si is formed (up to 70% of the total amount of copper). In analogous experiments without promoting agents Cu_3Si is not formed[116,131].

We believe that the change in the reactivity of the solid reactants (with and without promoting agents) during the synthesis of chlorophenylsilanes and the correlation between the relative content of Cu_3Si in the solid reactants and their reactivity (Fig. 3) also indicate an effect by the promoting agents on the chlorine transfer processes, which determine the course of the synthesis[131]. This is apparently of greatest significance in the initial most important period in the formation of the active form of the catalyst with participation of CuCl. By being involved in the formation of CuCl, the promoting agents thereby influence the phase transformations as a whole. The latter has an appreciable effect on the synthesis.

The fact that the presence of promoting agents in the solid reactant affects significantly the influence of the active source of chlorine (hydrogen chloride) introduced into the reaction zone (Fig. 4) constitutes yet another confirmation of the hypothesis that promoting agents influence the chlorine transfer processes. Fig. 4 shows that in the synthesis using a solid reactant without promoting agents the introduction of HCl can accelerate the formation of chlorophenylsilanes by a factor of 3.5, in the presence of zinc

only by a factor of 2, and in the presence of cadmium or a cadmium-zinc mixture the rate remains constant or falls[116].

Evidently the promoting agents involved in chlorine transfer facilitate the latter. It has been shown[108] that the characteristics of the reactions occurring when both promoting agents and HCl are introduced agree well with the chain mechanism of the direct synthesis.

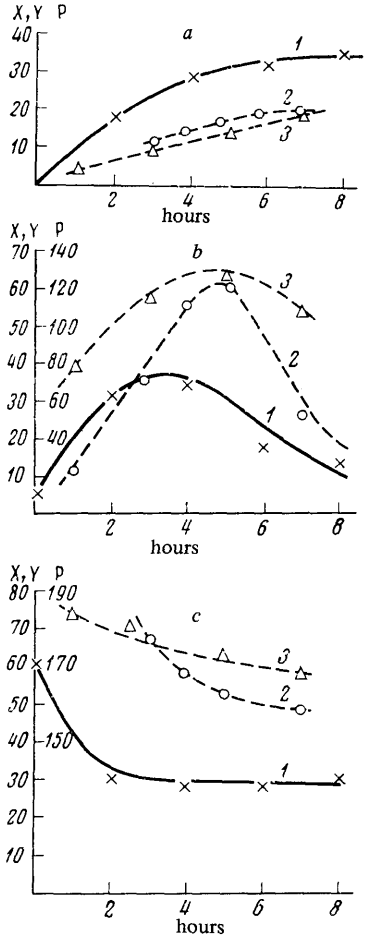


Figure 3. Phase composition of the solid reactants (curves *1*), their overall reactivity in the synthesis of chlorophenylsilanes (curves *2*), and their selectivity in the formation of dichlorodiphenylsilane (curves *3*): *a*) for a silicon–copper composition; *b*) for a silicon–copper–zinc oxide composition; *c*) for a silicon–copper–cadmium chloride composition; *X* = copper contained in Cu_3Si (per cent of total copper); *Y* = dichlorodiphenylsilane content in the mixture of reaction products (%); *P* = rate of formation of chlorophenylsilanes in the presence of 1 kg of solid reactant ($g\ h^{-1}$); the time from the start of synthesis is plotted as abscissa.

The involvement of promoting agents in chlorine transfer is also manifested in their influence on the synthesis of chlorophenylsilanes when another chlorine donor (trichlorosilane) is introduced[114]. The rate and selective reactivity in the direct synthesis of alkyl(aryl)chlorosilanes are to a large extent determined by the concentration and composition of the surface compounds $SiCl_n$. The effect of trichlorosilane reduces virtually to the involvement of the silyl radical $SiCl_3^{\cdot}$ in the process.

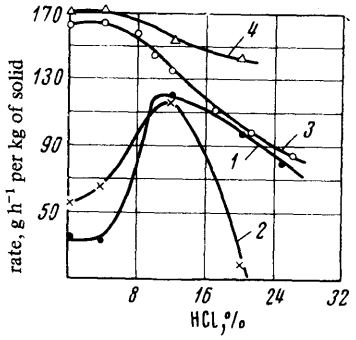


Figure 4. Effect of hydrogen chloride on the synthesis of chlorophenylsilanes in the presence of different solid reactants: *1*) without promoting agents; *2*) with zinc oxide; *3*) with cadmium chloride and zinc oxide; *4*) with cadmium chloride; the percentage of HCl in the mixture with chlorobenzene is plotted as abscissa.

In the absence of promoting agents, when the transfer of chlorine from chlorobenzene to silicon is relatively difficult, the introduction of trichlorosilane in all probability results in further formation of the compounds $SiCl_n$, corresponding to different degrees of chlorination, via the mechanism

$$-\overset{|}{\underset{|}{Si}}- \xrightarrow{SiCl_3^{\cdot}} -\overset{Cl}{\underset{|}{Si}}- + SiCl_{2\ ads} \cdot \qquad (7)$$

This results in an increase of the rate of formation of $C_6H_5SiCl_3$ and, what is most interesting, of $(C_6H_5)SiCl_2$ (Fig. 5). Fig. 5 shows that in the presence of $CdCl_2$ the rate of formation of $(C_6H_5)_2SiCl_2$ falls and the rate of formation of $C_6H_5Cl_3$ increases. This is consistent with the hypothesis that the presence of $CdCl_2$ has a favourable effect on the formation of the surface compounds SiCl via the mechanism

$$-\overset{|}{\underset{|}{Si}}- \xrightarrow[Cu,CdCl_2]{C_6H_5Cl} -\overset{Cl}{\underset{|}{Si}}- + \underset{\text{reaction products}}{C_6H_5^{\cdot}} \cdot \qquad (8)$$

In this case the involvement of the silyl radical apparently leads to an increase of the degree of chlorination via the mechanism

$$-\overset{Cl}{\underset{|}{Si}}- \xrightarrow{SiCl_3^{\cdot}} -\overset{Cl}{\underset{Cl}{Si}}- + SiCl_{2\ ads} \qquad (9)$$

and the formation of surface compounds which determine the synthesis of alkyl(aryl)trichlorosilanes. In conformity with these mechanisms, the formation of $C_6H_5SiCl_3$ with participation of trichlorosilane and in the absence of promoting agents is not accompanied by the liberation of the reaction products obtained from the phenyl radical:

$$SiCl_{2\ ads} + C_6H_5Cl \rightarrow C_6H_5SiCl_3 \cdot \qquad (10)$$

In the presence of $CdCl_2$ one mole of products from the phenyl radical is formed per mole of $C_6H_5SiCl_3$, which probably corresponds to the initial formation of SiCl with participation of chlorobenzene via mechanism (8).

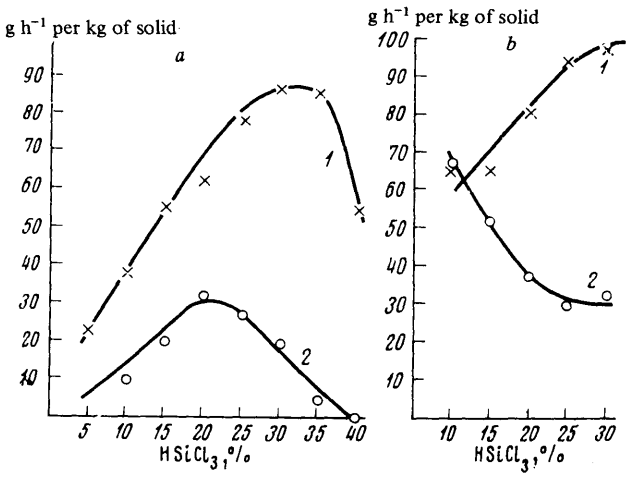


Figure 5. Rates of formation of trichlorophenylsilane (curves *1*) and dichlorodiphenylsilane (curves *2*) in synthesis in the presence of trichlorosilane; *a*) involving a silicon–copper reactant; *b*) involving a solid reactant with added cadmium chloride.

In their explanation of the mechanism of the action of promoting agents on chlorine transfer processes in the direct syntheses some investigators[116,117,188] began with the postulate that the transfer of chlorine to copper is appreciably hindered owing to the comparatively high strength of the bonds between the copper atoms in the crystal lattice, which can reach 81.1 kcal mole^{-1} (Skinner[8]) (in particular for powdered copper). It therefore appears useful to replace the single-stage formation of CuCl via reaction (5) by an energetically more favourable two-stage process, for example via the mechanism

$$RCl + M \rightarrow MCl + R^{\cdot}, \quad (11)$$
$$MCl + Cu \rightarrow CuCl + M. \quad (12)$$

Here the metal M must satisfy the following requirements: (a) it must be relatively readily atomised or must have a lower heat of sublimation than copper; (b) it must have a relatively high affinity for chlorine, which does not, however, exceed the chlorine–copper bond strength. These requirements are met, in particular, by Group II metals (zinc and cadmium), which, as already stated, are the most common and effective promoting agents in the direct synthesis[134,189–203]. Approximate calculations in the above studies showed that the formation of CuCl by reactions (11) and (12) with participation of promoting metals (including the processes where zinc or cadmium oxides or chlorides are introduced into the solid reactants) is preferred on energy grounds.

In the synthesis or chloromethylsilanes the use of the above promoting agents in combination with other procedures made it possible to achieve a virtually selective synthesis of the most valuable monomer, $(CH_3)_2SiCl_2$, the values of other reaction parameters being high. In the synthesis of chloroethylsilanes the content of $(C_2H_5)_2SiCl_2$ reaches 70 to 80% of the weight of the compounds formed[6].

Compared with the synthesis of chloromethylsilanes and chloroethylsilanes, the synthesis of chlorophenylsilanes at a high rate with the selective formation of $(C_6H_5)_2SiCl_2$ is most difficult, because the transfer of chlorine to copper and silicon is additionally hindered by the greater strength of the C–Cl bond in chlorobenzene[138] and the solid reactants consist of powdered mixtures instead of alloys[131]. For this reason the effect of the above Group II elements is particularly marked in this process[6,204] (see Table).

Effect of zinc, cadmium, and their compounds on the synthesis of chlorophenylsilanes.

Promoting agent	Rate of formation of mixture of chlorophenylsilanes, g h^{-1} per kg of solid reactant	Contents in mixture of reaction products, %			
		C_6H_5	$C_6H_5SiCl_3$	$(C_6H_5)_2$	$(C_6H_5)_2SiCl_2$
None	30–35	13–30	32–43	12–23	16–20
Zn or its compounds	50–80	14–17	26–32	2–3	45–50
Cd or its compounds	120–170	4–7	26–32	7–11	47–60
Mixture of Zn and Cd or their compounds*	150–200	2–7	4–15	0.3–1.0	70–80

* When combined promoting agents are used, the content of $(C_6H_5)_3SiCl$ in the reaction products reaches 5–9%.

The use of zinc and cadmium compounds as promoting agents made it possible for the first time to achieve more complex direct syntheses of organosilicon derivatives of heterocyclic compounds[202] and also of alkyl(aryl)chlorosilanes containing Si–C–Si linkages[203] with quite satisfactory results.

The regulation of the chlorine transfer processes and of the formation of the $SiCl_n$ surface intermediates by the introduction of promoting agents into the solid reactant and of chlorine donors into the gas phase made it possible to devise different versions of specific industrial synthesis[6].

The involvement of promoting agents in the chlorine transfer processes does not rule out the possibility of their influence on other stages of the process, in particular on the formation of the catalyst Si–C bond[116]. However, their effect on the chlorine transfer stage evidently plays a major role, because this state to a large extent determines the course of the entire direct synthesis.

Many important practical problems have been solved successfully on the basis of the ideas discussed above, whose development involved a major contribution by S. A. Golubtsov. This can serve as one of the criteria for the assessment of their validity and importance.

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