

DIRECT SYNTHESIS OF ORGANO-HALOGENOSILANES

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The first direct synthesis of organo-halogenosilanes was carried out successfully by Rochow although in the last century Wöhler and Combes came almost within reach of the direct synthesis when they reacted hydrogen chloride with silicon in the presence of copper, and only lack of experience and perseverance preventing them from finding the conditions for the reaction with methyl chloride.

MECHANISM OF ORGANO-HALOGENOSILANES SYNTHESIS

In our efforts to explain the mechanism of the direct synthesis we found that this is an extraordinarily complex process. For otherwise why should there be even nowadays so much effort expended on its study, as is witnessed by the hundreds of publications and patents (see the last comprehensive review¹). If we consider that we are dealing with a singular catalytic process in which one gaseous component reacts with two solid components and during which the contact mass (basically a mixture of silicon and copper) changes in composition, it is not very surprising to observe that particularly on the reaction mechanism of the direct synthesis so many different opinions have been forwarded and that its finer points are the subject of so many discussions. It seems to me that in our discussions one might well ask: "Were you there and did you see what the active sites and activated complexes looked like?" As is well known, even with simpler catalytic systems, after many years of work, we have not much certainty about the structure of the activated complexes on the surface of the solid catalyst. In the synthesis of ammonia, for example, which is known and studied for over 50 years, opinion is still divided over the question whether the adsorption of hydrogen or the surface reaction is the rate determining step. Heterogeneous catalysis as a system of metastable structures is still waiting for a unified theory and this obviously applies to its exceptionally complex case—the direct synthesis of organo-halogenosilanes; at least I hope that we all agree that this is a heterogeneous catalytic reaction. While accepting this state of things for the present we must also attempt to explain at least the "chemism" of the direct synthesis. I believe that in order to do so we must look for a sufficiently general view which will allow us to explain as many as possible of the experimentally determined facts.

All the results obtained from our study of the synthesis of organo-halogenosilanes over a considerable number of years confirm our view² which, however, we do not dare term a reaction mechanism, that the formation of silicon-containing as well as silicon-free products of the direct synthesis can be explained by reactions of groups or atoms formed by the dissociation of the

organic halide or gaseous admixtures, or by the decomposition of organic groups, adsorbed on the surface of the contact mass. Although it is not possible to exclude free-radical reactions at the high temperatures at which the direct synthesis is carried out, in our opinion these reactions predominantly lead to the formation of by-products.

From the study of the synthesis of methylchlorosilanes we have arrived at the following conclusions³: (i) In the synthesis, elementary copper acts as a catalyst in the same sense as in other catalytic reactions; (ii) The form in which copper is introduced to the contact mass is of no great consequence—with a mixture of pure silicon and finely divided copper we have obtained up to 90 per cent yields of dimethyldichlorosilane; (iii) If admixtures to the contact mass, recommended as promoters influence the process, then they decrease the conversion to dimethyldichlorosilane. The most effective admixture is aluminium, a small amount of which (up to 1 per cent) increases the overall reaction rate. The activity of the contact mass is, however, influenced significantly by trace amounts of elements built into the silicon lattice, as will be shown later; (iv) All gaseous admixtures have an adverse effect on the synthesis; although some of them increase to a certain extent the content of methyldichlorosilane this is always at the cost of conversion to dimethyldichlorosilane; (v) The optimum reaction temperature is from 270° to 290°C. At higher temperatures, as a result of the decomposition of methyl groups, there is increased formation of methyltrichlorosilane; and (vi) An increase in the pressure has a desirable effect on the synthesis and the optimum pressure is between 4 and 8 atm.

The fact that under suitable conditions dimethyldichlorosilane as a practically sole product of the reaction between methyl chloride and silicon is formed, and that the molar change of the remaining products also approximates unity, has enabled us to carry out kinetic studies of the direct synthesis in a static apparatus by following the change in pressure⁴. The best fit for our data was obtained by the equation:

$$r = \frac{k K_A p_A}{[1 + (K_A p_A)^{0.5} + K_R p_R]^2}$$

where r is the reaction rate [mole/h kg]; k , the reaction velocity constant [mole/h kg]; K_A , K_R , the adsorption coefficients [atm⁻¹] of methyl chloride and products, respectively; and p_A , p_R , the partial pressures of methyl chloride and products respectively [atm].

The above equation is also applicable to synthesis under higher pressure in a flow apparatus⁵. A third, independent, confirmation of the validity of this equation is seen in the fact that it is applicable in the description of the synthesis of methylbromosilanes⁶. In my opinion, the surprisingly excellent agreement of our results with those of Voorhoeve^{7, 8}, obtained in a flow apparatus with a fixed and fluidized bed of a silicon-copper alloy, is a sufficiently conclusive argument for the "chemism" of the synthesis which we have proposed. The first stage of the synthesis consists in the activated adsorption of the organic halide which probably dissociates on active sites of the contact mass. We may visualize that an active site consists of one copper and one silicon atoms. For the reaction to take place it is apparently neces-

sary for the copper and silicon atoms to come in as close a contact as is allowed by their atomic radii. In a mechanical mixture of the two substances this can be achieved, under reaction conditions, either by the diffusion of copper into the silicon lattice or vice versa, and in a copper-silicon alloy the necessary contact is achieved as a result of the decomposition of the inter-metallic compound. A further step which determines the rate of the process consists in a surface reaction, in which the organic group is transferred to the partially halogenated silicon, until finally a molecule of a volatile organo-halogenosilane is formed; the desorption of this compound forms the last stage of the synthesis.

SYNTHESIS OF ALKYLCHLOROSILANES

In research on the synthesis of methylchlorosilanes we are at the present time engaged in a study of the effect of definite amounts of small admixtures, incorporated into the atomic lattice of silicon, as these seem to have the decisive influence on the activity of the contact mass⁹. It seemed to us that the activity could be correlated with the semiconducting properties of silicon. A *p*-type semiconducting silicon, containing aluminium (10^{20} atoms per c.c. of silicon), which acts as an acceptor of electrons and reduces the electron density of the surface atoms of silicon, when reacted with methyl chloride gave a product which contained 90 per cent of dimethyldichlorosilane, already at 270°C. On the other hand, an *n*-type silicon, containing phosphorus (10^{19} atoms per c.c. of silicon), which acts as a donor and thereby increases the electron density of the surface atoms, reacted only at 350°C and the product contained only 60 per cent of dimethyldichlorosilane. Further, a semiconducting silicon prepared in an atmosphere of oxygen, and containing 10^{18} atoms of oxygen per c.c. of silicon (and it should be borne in mind that in the silicon lattice oxygen is not electroneutral) needed a temperature of 400°C for the reaction to take place. However, we had to abandon this attractive hypothesis. Experiments with a *p*-type, boron containing silicon, prepared with the same amount of boron and at the same conditions as the sample with aluminium, have shown that it did not react even at 400°C. This fact cannot be explained even by taking into consideration deoxidational properties of the mentioned admixtures, because, as contrary to phosphorus, boron also acts as a deoxidant. It seems, therefore, that the situation is much more complex and we shall have to proceed along different lines, perhaps by investigating the catalytic properties of aluminium.

In order to obtain more information on the mechanism of side reactions occurring in the direct synthesis of ethylchlorosilanes we thought it advisable to study the composition of the higher-boiling fraction of the reaction products and the structure of the individual components of this fraction. The fraction, which amounts to 10–15 per cent of the products, was separated into components by distillation and preparative gas-chromatography and the individual substances were identified mostly by comparing their i.r. and n.m.r. spectra with those of synthesized samples¹⁰.

As can be seen from *Table 1*, with the exception of dipropyldichlorosilane, all the isolated compounds are polymeric substances of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ type and especially of $\equiv\text{SiCH}_2\text{CH}_2\text{Si}\equiv$ type. The formation of disiloxane which has nothing in common with the mechanism of the synthesis can be explained

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Table 1. Compounds isolated from the higher-boiling fraction of the products of the direct synthesis of ethylchlorosilanes

Compound	wt(%)	Compound	wt(%)
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{H}-\text{Si}-\text{O}-\text{Si}-\text{Cl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	1.3	$\begin{array}{c} \text{Cl}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3 \\ \text{CH}_2\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{Cl}_2\text{Si} \quad \text{SiCl}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CH}_2 \end{array}$	33.1
$(\text{C}_3\text{H}_7)_2\text{SiCl}_2$	2.2		
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{Cl}-\text{Si}-\text{O}-\text{Si}-\text{Cl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	4.3	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{Cl} \\ \quad \\ \text{Cl}-\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}-\text{Cl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	20.9
$\begin{array}{c} \text{H} \quad \quad \quad \text{Cl} \\ \quad \quad \quad \\ \text{Cl}-\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}-\text{Cl} \\ \quad \quad \quad \\ \text{Cl} \quad \quad \quad \text{Cl} \end{array}$	6.8	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{Cl}-\text{Si}-\text{CH}_2\text{CH}_2-\text{Si}-\text{Cl} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}$	5.2

by the presence of the moisture or of air in ethyl chloride. The disilethylene types of compounds contain the same grouping as that formed by the reaction of 1,2-dichloroethane with silicon. The formation of a disilethylenic type of compound from a reaction of ethyl chloride with silicon can be assumed to proceed in the following manner. On the surface of the contact mass a hydrogen atom can split off from the adsorbed ethyl radical with the formation of an ethylenic biradical. Another possible explanation is based on the conception that a chloroethyl radical ($\cdot\text{CH}_2\text{CH}_2\text{Cl}$) can be formed by a reaction of an adsorbed ethyl radical with ethyl chloride. The chloroethyl radical can then react in a similar manner as 1,2-dichloroethane. The formation of propyl radicals can be assumed to be the result of synthetic reactions of adsorbed radicals.

SYNTHESIS OF ARYLHALOGENOSILANES

Not long ago we also started to study the direct synthesis of phenylchlorosilanes. This is a more difficult case because in view of the low reactivity of chlorobenzene the reaction temperatures must be above 450°C , with the result that the selectivity of the reaction is decreased (in this case we have obtained not more than 70 per cent conversion to phenylchlorosilanes). Triphenylchlorosilane to the extent of 1–2 per cent is also formed and the by-products consist mainly of benzene, tetrachlorosilane, and biphenyl. With increasing temperatures the content of biphenyl decreases whereas the contents of benzene and tetrachlorosilane increase. It appears that, as in the synthesis of alkylchlorosilanes, all the products are formed by parallel reactions (*Figure 1*). The influence of admixtures on the synthesis of phenylchlorosilanes is analogous to that in the reaction of methyl chloride, but in view of the higher temperature it is even more complex¹¹.

In connection with our work on the mechanism of direct synthesis we have also been interested in the question of how a substitution on the aromatic

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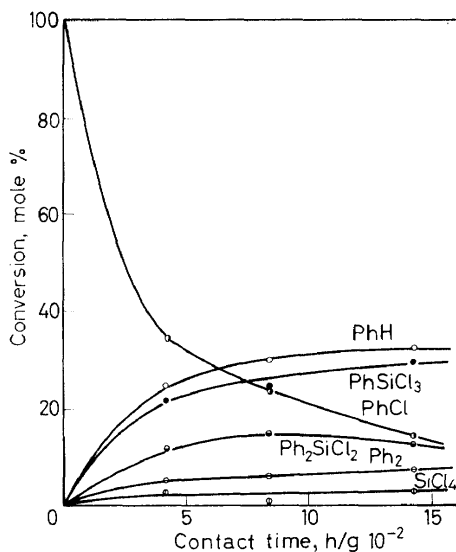
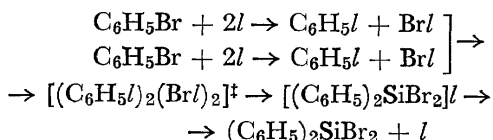


Figure 1. Direct synthesis of phenylchlorosilanes: Effect of contact time on conversion

nucleus influences the reaction rate. For studying this type of reaction we have selected the more reactive alkylaromatic bromides. As a first step in the quantitative evaluation of the effect of substituents on the aromatic nucleus we have studied the kinetics and material balance of the reaction of bromobenzene with silicon¹². From the kinetic analysis it follows that the rate determining step is a surface reaction of bromobenzene with the contact mass. Deviations from expected linear relationships together with estimates of the probable value of the standard change in enthalpy of adsorption of bromobenzene have enabled us to select from eight possible kinetic mechanisms the two most probable cases between which a decision cannot be made on the basis of the available kinetic data. One of these mechanisms implies that bromobenzene is adsorbed with dissociation and the other that diphenyldibromosilane is formed by a reaction in which two molecules of bromobenzene react consecutively or simultaneously with a silicon atom. It seems that the most probable is that kinetic mechanism according to which two molecules of dissociatively adsorbed bromobenzene take part in the surface reaction. The formation of a molecule of diphenyldibromosilane can then be expressed as in the following scheme:



where $2l$ denotes an active double site.

As is to be expected, the course of reactions of alkylaromatic bromides is more complicated than that of phenyl halides, because decomposition reactions occur in a larger measure in the latter than in the former case. Kinetic

studies on the reactions of *o*, *m*, and *p*-bromotoluenes and higher alkylphenylbromides are in progress. In preliminary work we have verified that isomerization of bromotoluenes and of formed tolylbromosilanes is negligible¹³.

SIDE REACTIONS BY DIRECT SYNTHESIS

In the last part of this lecture I wish to report on the results of our studies on the properties of the contact mass and of the non-volatile silicon-free products, which are formed in the direct synthesis of phenylhalogenosilanes. The development of the texture of the contact mass during the reaction has been investigated by measuring its bulk density, its specific surface area (by the BET method); for selected samples we have also determined the complete adsorption isotherms of benzene in a gravimetric apparatus containing silica spirals¹⁴. On comparing the results of reactions of chlorobenzene and bromobenzene at approximately the same degree of conversion (470° and 370°C) the kinetic dependences (*Figure 2*) reveal a basic difference

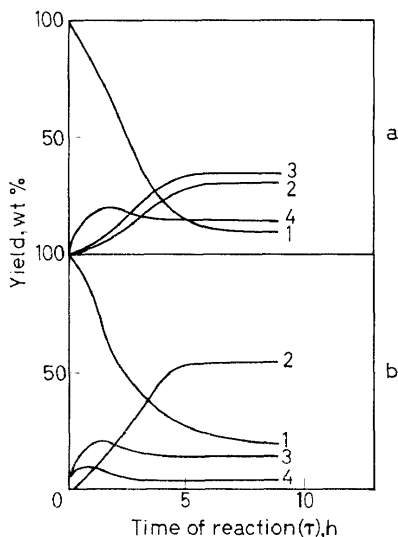


Figure 2. Kinetic dependences of the direct synthesis of phenylhalogenosilanes (a) Phenylchlorosilanes: 1, chlorobenzene; 2, diphenyldichlorosilane; 3, phenyltrichlorosilane; 4, benzene. (b) Phenylbromosilanes: 1, bromobenzene; 2, diphenyldibromosilane; 3, phenyltribromosilane; 4, benzene

in the selectivity of both reactions, which is reflected foremostly in the value of the ratio $\text{PhSiX}_3/\text{Ph}_2\text{SiX}_2$. For both processes it is to be expected that the formation of PhSiX_3 is dependent on the extent of carbon deposits on the surface. The different development of the texture is apparent from *Figure 3*. It can be seen that practically throughout the investigated range there is a distinct analogy between the carbon content of the contact mass (a), the bulk and specific densities (b and c), and the specific surface areas (d).

The decrease in the density as well as the increase in the surface area can be taken in the case of the reaction with chlorobenzene as a direct consequence of the formation of decomposition products. Carbonaceous decomposition products have an exceptionally well developed microporous structure

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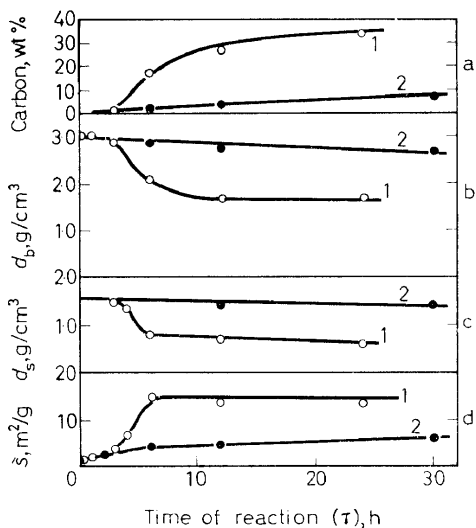


Figure 3. Basic parameters of the textures of the contact mass in the course of the direct synthesis of phenylhalogenosilanes [a, carbon content; b, bulk density; c, specific density; d, specific surface area. 1, phenylchlorosilanes; 2, phenylbromosilanes]

(specific surface area S 200 m^2/g , effective non-corrected radii of most frequent pores \bar{r}_k 15 Å), in comparison with which the structure of copper and silicon can be neglected.

An answer to the question whether the different behaviour of chlorobenzene is due to the nature of the halogen atom or to the different temperature can be obtained from Figure 4. An increasing reaction temperature in

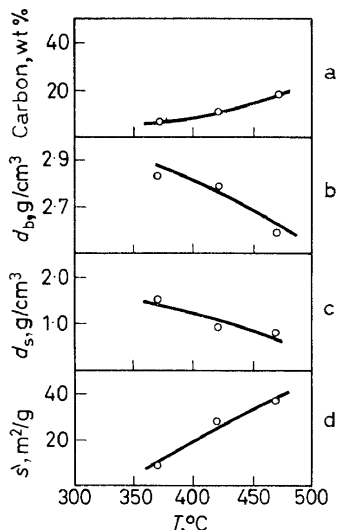


Figure 4. Temperature dependences of the texture parameters of the contact mass from the direct synthesis of phenylbromosilanes (time of reaction 27 h) [a, carbon content; b, bulk density; c, specific density; and d, specific surface area]

the direct synthesis of phenylbromosilanes produces changes in the texture parameters; the carbon content and thereby also the specific surface area increases, the specific and bulk densities decrease. However, even at 470°C the degree of carbonization is only two-thirds of that found in the direct synthesis of phenylchlorosilanes (Table 2).

Table 2. Direct synthesis of phenylhalogenosilanes: Main characteristics of contact mass

Sample No.	Reaction component	T (°C)	τ (hr)	C (wt,%)	nH/6C
1	C ₆ H ₅ Cl ^a	470	24	33.9	3.91
2		510	32	29.6	3.90
3		550	28	27.9	3.21
4	C ₆ H ₅ Br ^b	370	30	7.2	5.22
5		420	30	11.9	4.62
6		470	27.5	18.9	4.42

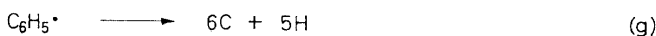
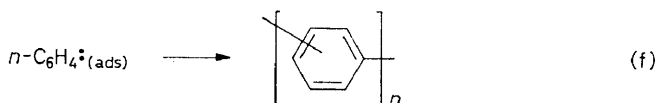
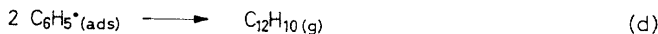
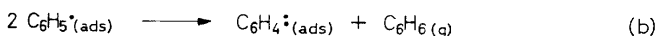
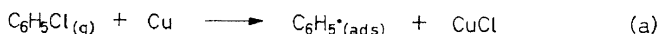
^a F/W = 0.12 g/hg_{CM}

^b F/W = 0.18 g/hg_{CM}

As a result of the smoother course of the synthesis of phenylbromosilanes the plugging of the pores by decomposition products is also less; in view of the greater strength of the Si-Cl bond, higher local overheating is encountered in the formation of this bond than in the formation of Si-Br bonds.

Hydrogen chloride, contrary to expectation, reduces the formation of benzene in the direct synthesis of phenylchlorosilanes. The carbon content of the contact mass is in this case about 10 per cent and as a result of this, the changes in the values of the texture parameters are small. It is probable that hydrogen chloride reacts with the dissociation products of chlorobenzene, which are bonded to the surface of the contact mass, and transfers them back to the gaseous phase. This means, in effect, that the surface of the contact mass is being purified during the synthesis.

Considerable amounts of silicon-free by-products are formed in the synthesis of phenylchlorosilanes. These by-products are of two different kinds. The first kind consists of low-boiling aromatic substances, mainly benzene and to a lesser degree biphenyl, and diphenylbenzenes. The second kind, however, consist of non-volatile carbonaceous substances, which are deposited



on the contact mass; they increase considerably the volume of the mass during the reaction and, obviously, decrease its reactivity.

Some time ago we had proposed a reaction scheme¹⁵, based on the interaction of adsorbed phenyl radicals which are formed by the dissociation of halogenobenzenes on copper (illustrated on page 320).

During the synthesis, adsorbed radicals are removed from the surface of copper foremostly by reactions with active sites on silicon. In addition, mutual reactions between adsorbed components (b, c) can also take place. These relations also explain the formation of biphenyl and diphenylbenzene (d, e). However, equations (b) and (c) may also represent sources of non-volatile silicon-free products.

Adsorbed bi- and tri-radicals can also be bonded directly to the surface of the contact mass and they also react among themselves with the formation of polymers (f); even a more thorough decomposition of benzene nuclei, usually described by means of equation (g), cannot be excluded.

Already a simple calculation indicates that only a small fraction of the adsorbed groups can be bonded to the surface. If the content of decomposition products in the contact mass is 40 per cent by weight, radicals with diameter 40 Å would form a monomolecular layer on a surface area exceeding 1000 m²/g. Since the specific surface area of pure copper is of the order of tenths of m²/g, it is clear that the large majority of radicals must leave the copper surface. The ratio of hydrogen to carbon in the non-volatile products can be expressed as $nH/6C$ where n usually approximates to 4. Decomposition products isolated from the contact mass by leaching it alternately with a 5 per cent sodium hydroxide solution and nitric acid¹⁶, decomposed in a nitrogen atmosphere at elevated temperature only very slowly (at 600°C n falls to about 3). A comparison of i.r. spectra of synthetic polyphenyl and of decomposition product of the direct synthesis of phenylchlorosilanes has revealed that the decomposition products consist foremostly of polyphenyl, with the majority of bonds in para positions, to a lesser degree in ortho positions and with only a slight amount of bonds in meta positions. Also the thermal stability of synthetic polyphenyl was found to be similar to that of the decomposition products.

Further interesting information has been obtained from the evaluation of texture parameters from the synthesis of phenylbromosilanes (*Figure 5*); the desorption branch of the isotherm indicates that at 370°C the substances have a very fine microstructure (a) and at 420°C we can clearly distinguish between two forms, differing in the size of pores (b). The diameter of the pores of the first form is in the range of $\bar{r}_k < 10$ Å, in which the Kelvin equation loses its physical meaning, whereas the second form corresponds to values of $\bar{r}_k = 15$ Å. At 470°C only the second form exists (c), and the substances are practically identical in structure with the contact mass from the synthesis of phenylchlorosilanes, with the decomposition product of this reaction as well as with synthetic *p*-polyphenyl (d). In order to clarify the process of formation of the decomposition product we have studied the morphology of these substances by means of electron microscopy. The contact mass obtained after the direct synthesis of phenylchlorosilanes contains a considerable fraction of larger particles, probably copper, which are covered by film-like or globular formations (*Figure 6*). In addition to this

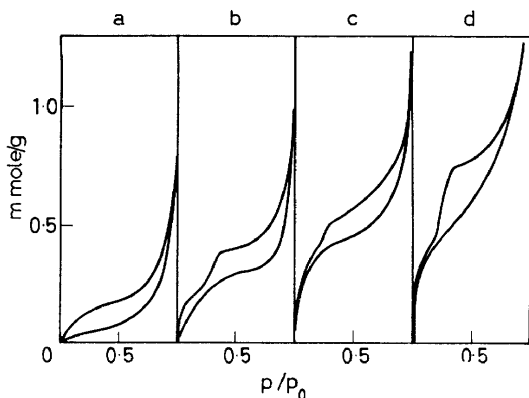


Figure 5. Adsorption isotherms of benzene (20°C) on contact masses (cf. Table 2) and synthetic *p*-polyphenyl [a, sample 4; b, sample 5; c, sample 6; d, synthetic *p*-polyphenyl heated in nitrogen stream at 470°C.]

there have also been found isolated, I shall term them "free", decomposition products, which have apparently at a certain stage of their development broken off from the copper particles and thus freed their surface for taking part again in the reaction.

Selective electron diffraction has shown that these substances are definitely amorphous and that morphologically and as regards dispersion efficiency, they are similar to synthetic *p*-polyphenyl. Investigations of samples of contact mass from the synthesis of phenylbromosilanes have confirmed these results; after a reaction at 370°C a small amount of decomposition products, characterized mainly by a more developed surface structure, has been found. The situation was different when the reaction was carried out at 420° and 470°C, the amount of decomposition products increased sharply and globular formations were found (Figure 7). However, the number, the frequency of occurrence and the voluminous development of the globules were all less than for contact masses from the synthesis of phenylchlorosilanes.

On the basis of the presented evidence the formation of non-volatile, silicon-free decomposition products can be characterized as a process of mutual interactions of dissociatively adsorbed products of halogenobenzenes, the most likely one being the biradical $C_6H_4\cdot$; decomposition reactions probably take place foremostly on copper particles. In the initial phase the polymer apparently forms a somewhat permeable coating on the particle, later it loosens and gradually folds up creating free globule formations, and freeing thereby the surface of the copper particle. As I have already mentioned the i.r. spectra indicate that the greater part of the bonds is in the *p*-position. This is supported also by what we have learnt of the influence of a non-reactive methyl group on the extent of carbon deposits on the contact mass. Under comparable conditions there is practically no difference in the synthesis of phenylbromosilanes and of *m*-tolylbromosilanes, whereas in reactions leading to *o*-tolylbromosilanes the amount of decomposition products is less by about a third and in reactions leading to *p*-tolylbromosilanes it is reduced by more than a half. Thus in the decomposition of bromobenzene

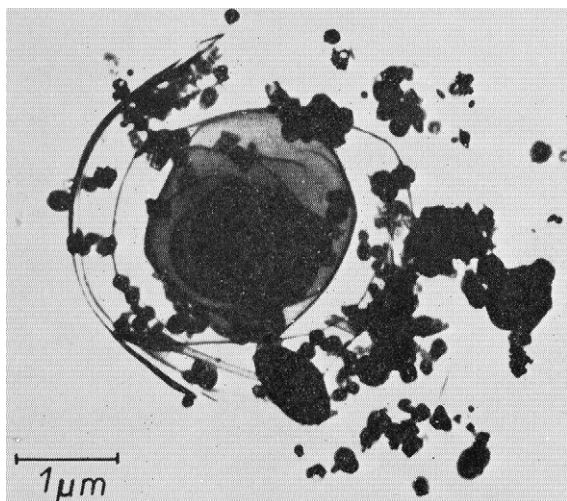


Figure 6. Non-volatile decomposition products deposited on the contact mass after the direct synthesis of phenylchlorosilanes (cf. *Table 2*)

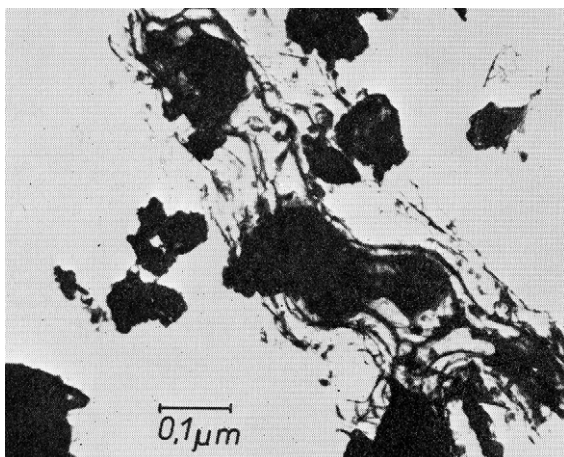


Figure 7. Non-volatile decomposition products deposited on the contact mass after the direct synthesis of phenylbromosilanes (cf. *Table 2*, sample 6)

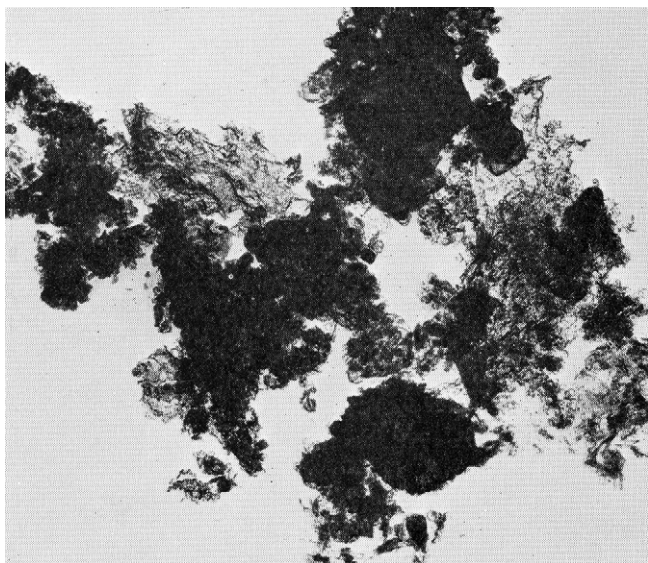


Figure 8. Non-volatile decomposition products deposited on the contact mass after the direct synthesis of methylbromosilanes (T 320°C.)

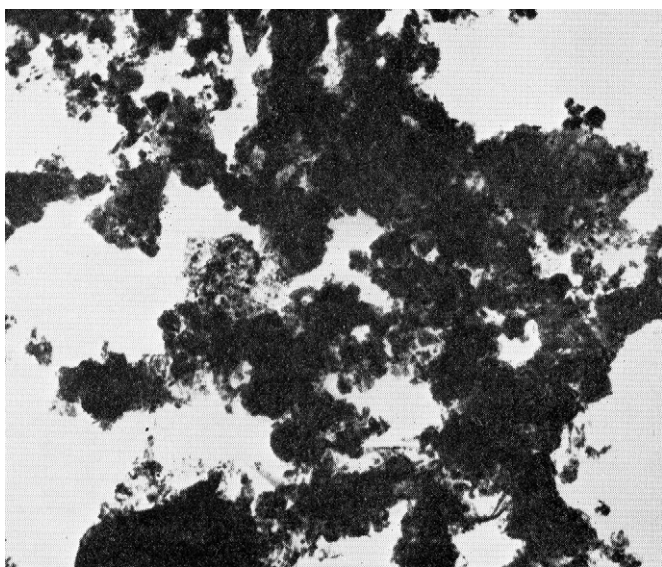


Figure 9. Non-volatile decomposition products deposited on the contact mass after the direct synthesis of methylchlorosilanes (T 360°C.)

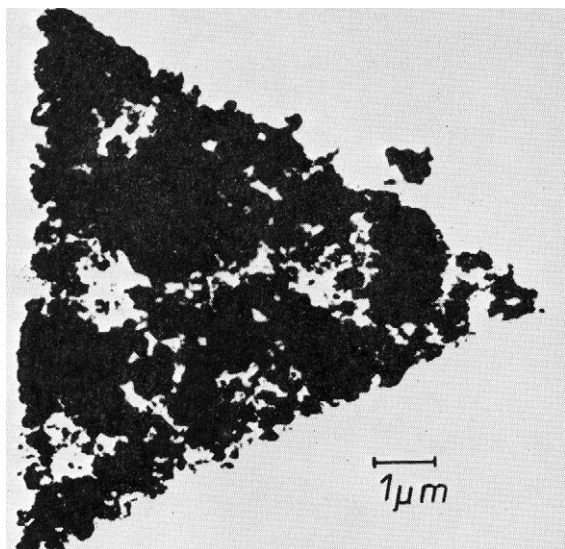


Figure 10.-12. Particles of silicon carbide in the contact mass after the direct synthesis of phenylchlorosilanes (cf. Table 2, sample 1)

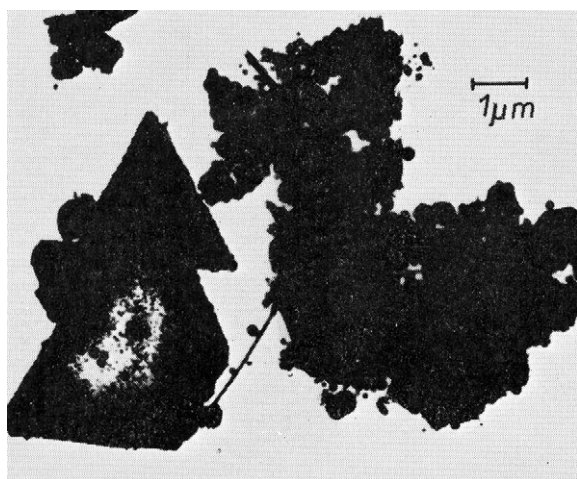


Figure 11

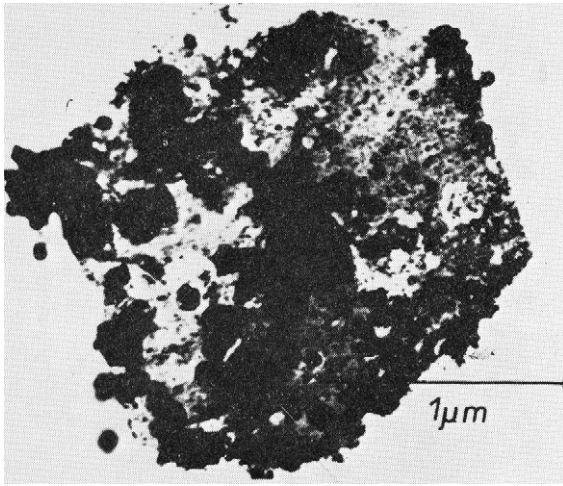


Figure 12

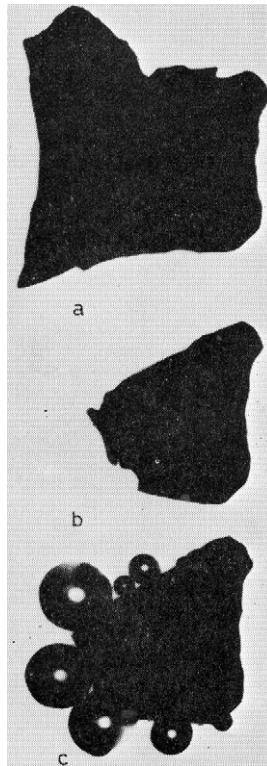
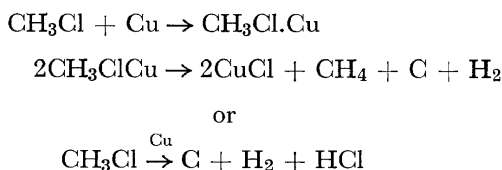


Figure 13. Influence of grinding on the reactivity of contact mass particles [(a) original particle in 5 per cent sodium hydroxide; (b) selected fragment with newly formed surface; (c) formation of hydrogen bubbles on the newly formed surface parts after the action of 5 per cent sodium hydroxide]

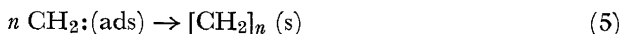
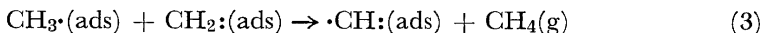
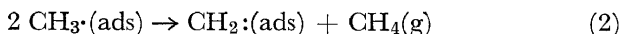
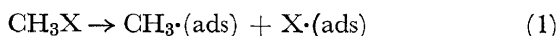
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on copper the chain formation in the product is effected mainly by para positions and to a lesser degree by ortho positions.

Also in the direct synthesis of methylhalogenosilanes silicon-free products are formed¹⁷ by two distinct groups of side reactions. The products consist on the one hand of volatile substances, such as methane, ethane, ethylene, hydrogen, hydrogen chloride and certain higher hydrocarbons, whereas on the other hand non-volatile carbonaceous residues are deposited on the contact mass. The mechanism of formation of these products is usually explained^{18, 19} by the following equations:



However, the results of our study of the problem²⁰, in which we have applied methods analogous to those mentioned in the case of phenylhalogenosilanes, indicate that this explanation is incorrect; it may be assumed that the processes leading to the formation of the mentioned products are analogous to those occurring in the synthesis of phenylhalogenosilanes:



As the first of the series of successive processes we can consider the dissociative sorption of the methyl halide (equation 1); the adsorbed radicals can react not only with the activated sites on the silicon surface, that means that they can take part not only in the reaction of direct synthesis, but

Table 3. Direct synthesis of methylchlorosilanes: Main characteristics of contact mass

T (°C)	τ (h)	Silicon conversion (wt %)	Ratio $\text{CH}_3\text{SiCl}_3/(\text{CH}_3)_2\text{SiCl}_2$	Carbon (%)	Mole ratio H/C	Surface area (m ² /g)	Density(g/cm ³)	
							Bulk	Specific
320	2	5.1	0.33	0.26	5.9	3	1.45	2.48
	8	20.7	0.17	0.87	2.6	7	1.41	2.55
	30	60.4	1.2	9.07	1.3	44	0.45	2.57
360	2	4.9	1.87	0.79	2.0	2	1.35	2.43
	10	22.0	0.62	1.63	1.5	6	1.23	2.49
	30	64.2	1.2	10.18	0.7	45	0.78	2.75
400	2	5.1	1.27	0.93	2.7	3	1.38	2.47
	10	22.9	2.5	2.88	1.1	7	1.16	2.51
	30	53.6	3.9	15.94	0.5	50	0.55	2.48

also in a number of mutual interactions (equations 2–5). This is in fact an analogy of disproportionation (equations 2, 3) and recombination reactions of free radicals (equation 4). The chain formation of adsorbed radicals (equation 5) represents a hitherto unconsidered possibility for explaining the deposition of silicon-free decomposition products on the contact mass. The branching of polymethylene chains can be explained by the reaction of ter-radicals according to equation 3. Our conceptions are also supported by the presence of substances of the type $\equiv\text{Si}(\text{CH}_2)\text{Si}\equiv$ in the products of the synthesis of methylchlorosilanes and by the formation of the already mentioned substances $\equiv\text{Si}(\text{CH}_2\text{CH}_2)\text{Si}\equiv$ in the products of the synthesis of ethylchlorosilanes, and further by the presence of polymethylene compounds, containing hydrogen and carbon in the ratio of 2 H/C, which have been found by Long and coworkers²¹ in the products of thermal decomposition of methyl-metallic compounds at temperatures of about 300°C (ref. 6).

A comparison of the time-course of the synthesis of methylchlorosilanes (Table 3) at temperatures from 320 to 400°C, and of methylbromosilanes at temperatures from 280 to 360°C, with the main textural parameters of the corresponding contact masses actually reveals that when the reaction temperature is increased, the ratio of $\text{CH}_3\text{SiX}_3/(\text{CH}_3)_2\text{SiX}_2$ also increases, and that the carbon and hydrogen content can easily be correlated with the temperature and therefore also with the ratio of $\text{CH}_3\text{SiX}_3/(\text{CH}_3)_2\text{SiX}_2$. A direct proportionality is found only between the carbon content and the surface of the contact mass, the development of which can be attributed practically only to the silicon-free decomposition products; variations of the bulk density illustrate the well known growth of the volume of the contact mass during the reaction, and the specific densities indicate that the rate of carbon deposition is such that it approximately compensates the decrease in the content of silicon, *i.e.* of the lighter component in the contact mass.

With the exception of the highest reaction temperatures, in the initial period a larger amount of methyl-trihalogenosilanes is formed, and only later are the products enriched by dimethyldihalogenosilanes. This can be explained by the gradual removal of the oxidic layer from the silicon. When silicon has reacted to a higher degree the compositions of the main products change again in favour of methyltrihalogenosilanes. The higher reactivity of methyl bromide is of significance only in that higher conversions are attainable at temperatures lower than 300°C, and as regards selectivity that the content of dimethyldibromosilane is higher (Table 4).

Infrared spectra of samples of the contact mass, from which about 80 per cent of silicon and copper have been removed carefully, have definitely proved the presence of methylene as well as some methyl groups. An investigation of equilibrium loss in weight of a commercial polyethylene in an atmosphere of nitrogen has shown that even this not much cross-linked polymer is practically stable almost up to 300°C; further increasing the temperature leads to considerable losses in weight but the composition of the remaining fraction corresponds to the ratio 2 H/C.

In the synthesis of methylbromosilanes the ratio of H/C is higher than in the synthesis of methylchlorosilanes. This is because in analogy with the synthesis of phenylhalogenosilanes; much higher local overheating of the

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reacting particles is to be expected in the reaction of methyl chloride. Also, higher reaction temperatures result in decreasing hydrogen contents in all the mentioned cases; the decrease is more pronounced at higher reaction temperatures.

Table 4. Direct synthesis of methylbromosilanes: Main characteristics of contact mass

T (°C)	τ (h)	Silicon conversion (wt %)	Ratio CH ₃ SiBr ₃ /(CH ₃) ₂ SiBr ₂	Carbon (%)	Mole ratio H/C	Surface area (m ² /g)	Density(g/cm ³)	
							Bulk	Specific
280	2	3.1	0.45	0.79	3.6	4	1.37	2.44
	10	15.3	0.22	1.57	2.5	9	1.13	2.46
	30	47.6	0.37	3.44	2.2	18	0.81	2.03
320	2	3.6	0.62	0.67	3.6	3	1.36	2.48
	10	20.2	0.45	1.91	2.2	9	1.28	2.46
	30	58.4	0.62	7.24	1.7	48	0.47	2.41
360	2	3.6	0.87	0.78	2.8	3	1.50	2.48
	10	19.1	0.42	1.71	2.5	6	1.32	2.32
	30	50.7	2.2	10.57	1.0	48	0.75	2.28

The carbonaceous deposits on the contact mass have been investigated by means of electron microscopy and it has been found that it undergoes morphological changes during the synthesis. At lower temperatures the formations are quite transparent (*Figure 8*) and similarly as with the decomposition products from the synthesis of phenylhalogenosilanes, here also we find film-like formations containing particles of the contact mass, as well as free globules, which are formed, apparently, by the gradual freeing and folding up of the primary film-like formations. The decreasing transparency of the organic particles is closely related with their gradual destruction, i.e. with the decreasing value of the H/C ratio (*Figure 9*). Electron diffraction of the organic residues has shown that substances are definitely amorphous. However, our present state of knowledge does not enable us to decide whether the removal of hydrogen from the decomposition products is due to thermal decomposition or to interactions of polymethylene with some components of the reaction medium.

In contact masses from the synthesis of phenylchlorosilanes there have also in rare cases been found objects of remarkably regular geometrical form²². The frequency of occurrence of these objects increased slightly with the reaction temperature and time. The most frequently found form was that of an equilateral triangle (*Figure 10*), less frequent were triangular forms with chamfered apexes (*Figure 11*), and in rare cases there have also been found particles of almost regular hexagonal form (*Figure 12*). By means of selective electron diffraction we were able to determine the interplanar distances, which were compared with sets of interplanar distances for possible substances. The results indicate that the substance in question is probably a monocrystal of the hexagonal modification of silicon carbide.

In the reacted contact masses from the synthesis of methylhalogenosilanes²³ we have not been able to detect monocrystals of silicon carbide as in the case of phenylchlorosilanes²². However, it is not improbable that the slow formation of this compound participates in such processes. The most acceptable possibility seems to be the thermal decomposition of organohalogenosilanes, which presumably, proceeds²⁴ to a considerable extent at

600°C, but the interaction of the products of this decomposition with carbon²⁵ or carbonaceous decomposition products cannot be excluded. We believe that the covering of particles of contact masses by silicon carbide deposits is, in addition to the above mentioned formation of silicon-free polymers, closely connected with the decrease in the activity of the contact masses during the direct synthesis.

It is difficult to support this view with incontestable evidences, because the reacted contact masses mentioned represent an extraordinarily complicated system, containing as a rule some (*ca.* 0.5 wt%) silicon carbide from the pure silicon used initially. But all the same there are some arguments which strengthen such an opinion.

After removing the free silicon and copper by successive treatment of contact masses with dilute (5 wt%) sodium hydroxide and nitric acid the resulting simplified residues still contain a certain amount of both silicon and copper, which are detectable not only by analytical methods but also by x-ray phase analysis. Approximate estimations indicate that after 30 h of reaction, up to one-fifth of the contact mass can become blocked in this way. And if we consider that this concerns samples in which about 50 per cent of silicon has reacted, the agreement of these results with the usually observed maximum degree of silicon utilization (70 to 80 per cent) can be to a certain extent taken as an indication of causal relationship.

The view that the mentioned insoluble fraction of silicon and copper are of stratified structure is also supported by the results of two qualitative experiments²³. The first of these is based on the fact that silicon carbide is, at normal temperatures, insoluble in dilute solutions of alkali hydroxides and mineral acids, but is soluble in a mixture of hydrofluoric and nitric acids. When the samples were etched by this mixture, the resistance of silicon to alkalis and copper to acids was remarkably quickly destroyed and we could observe how the golden-red surface of copper particles then gradually appeared from under the dissolving greyish-black surface layers. In the second experiment we removed partially the inert surface layers by careful grinding. In *Figure 13* it can be seen how an originally insoluble particle of silicon is, after splitting, attacked by dilute sodium hydroxide only on the newly formed parts of surface.

At present further investigations are in progress to gain a better understanding of this interesting problem.

In conclusion, I would like to express my thanks to my present and past coworkers in this field of organo-silicon chemistry, particularly to J. Joklík, F. Jošt, M. Kraus, O. Kruchňa, J. Rathouský, L. Scháněl, K. Setínek, and M. Vavruška.

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