

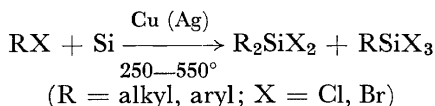
# ON THE MECHANISM OF THE DIRECT SYNTHESIS OF ORGANOHALOGENOSILANES

VLADIMÍR BAŽANT

*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences,  
Prague, Czechoslovakia*

I think it necessary to survey briefly the present, not infrequently contradictory opinions on the reaction mechanism of the direct synthesis of organohalogenosilanes.

The first attempt to explain the mechanism of the direct synthesis of methylchlorosilanes was made by their discoverer, Rochow, and his co-worker Hurd in 1945. According to them in the first stage methyl chloride reacts with copper with the formation of cuprous chloride and methyl copper:



Cuprous chloride can transfer chlorine to silicon and in this way form on its surface an active site which can react with methyl copper or with a free methyl radical resulting from its decomposition. The process proceeds until a molecule of volatile methylchlorosilane is formed. Copper therefore has two functions in the synthesis: in the first place it reacts with methyl chloride to form cuprous chloride which activates silicon, and in the second place it prolongs the life time of methyl radicals in the reaction space by bonding them temporarily. Recently, Krahé and Rochow replaced copper by gold as the catalyst, and observed the formation of volatile and unstable organic compounds of gold.

Several objections were subsequently raised against the radical mechanisms. One of the most important arguments is the fact that the direct synthesis can be carried out very selectively, up to 90 per cent of dimethylchlorosilane can be obtained. Such high selectivities have not so far been observed in free radical reactions. Another objection is that the direct synthesis of some alkyl- and alkenyl-chlorosilanes can be carried out at temperatures below 260°, whereas it is only at this temperature that the chlorination of silicon by cuprous chloride begins.

The concept of the formation of an organic copper compound cannot be applied to the synthesis of other alkylhalogenosilanes and of arylhalogenosilanes where the organic copper compounds formed would have a very short, if any, life-time. Further, the participation of free radicals in the alkylation of silicon cannot be reconciled with the fact that considerable amounts of disilethylene type compounds are formed in the ethylchlorosilane synthesis, because this would require the existence of free biradicals in rather high concentration. Furthermore, we have proved that in the

direct synthesis of phenylchlorosilanes, free phenyl radicals exist only in negligible amount. When free phenyl radicals generated by the decomposition of benzil were allowed to react with chlorobenzene mainly chlorobiphenyls were formed, whereas in the direct synthesis higher-boiling hydrocarbons consisted mainly of biphenyl. This is also in agreement with the results of studies on the effect of nitrous oxide on the synthesis of methylchlorosilanes, from which it follows that free methyl radicals do not participate in the alkylation reaction. We have proved that methyl groups appear to be in two forms: one which reacts easily with NO and yields hydrocarbons, and the other one which yields methylchlorosilanes. From *Table 1*, it is

*Table 1.* Comparison of critical NO:CH<sub>3</sub>Cl ratios with fractions of CH<sub>3</sub>Cl forming decomposition products

Temperature °C	NO:CH <sub>3</sub> Cl ratio	Fraction of CH <sub>3</sub> Cl
350	0.20	0.19
400	0.30	0.28
470	0.60	0.53

apparent that the ratio NO/CH<sub>3</sub>Cl, at which the synthesis is inhibited, corresponds very well to the fraction of methyl chloride which is converted into hydrocarbons. It is only reasonable to believe that the other fraction of methyl groups is adsorbed on the surface of the contact mass.

From these results followed the suggestion of a chemisorption mechanism for the direct synthesis, which was proposed simultaneously by us and, independently, by Trambouze in France and Klebanskij and Fichtengolc in the USSR. We should also note in this connection the work of Voorheove in Holland and that of Golubtsov and co-workers in the USSR.

The mechanism is in principle based on the theory of heterogeneous catalytic reactions: the first, a rapid stage, is the adsorption of the organic halide on the contact mass, the active sites of which can be considered as being composed of one silicon and one copper atom; the next stage is slow, and therefore the rate determining step—the surface reaction with silicon of the adsorbed organic halide. The last stage, again a fast one, is the desorption of the volatile organohalogenosilane formed. I shall not describe in detail the discussions and indirect experimental proof of the details of the course of these reaction stages: whether the reactivity of the contact mass is due to the formation of the intermetallic compounds Cu<sub>3</sub>Si, whether the organic halide is adsorbed with or without dissociation, whether the organic group is adsorbed on silicon and the chlorine atom on copper or vice versa, whether the reactivity of the organic halide can be correlated with its polarity or polarizability, what is the role of various promoters or inhibitors, that is elements, present in technical grade silicon or added in various forms to the contact mass, whether vacant *d*-orbitals of silicon play a role in the formation of the activated complex and so on.

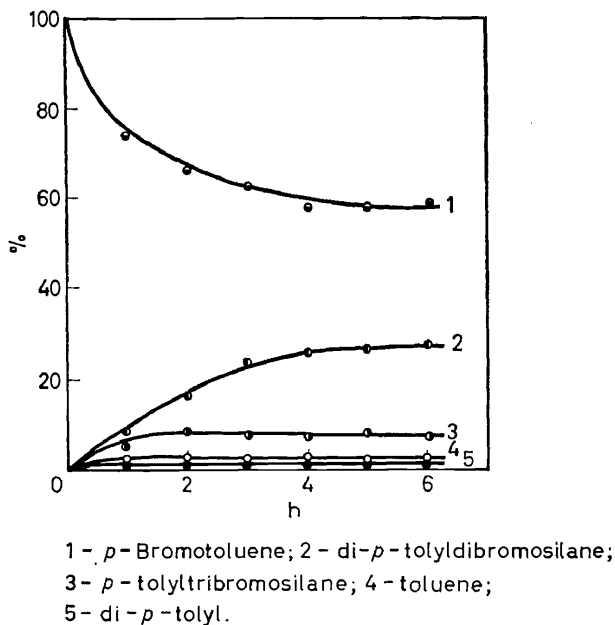
I have already had the opportunity to report in our Prague symposium on our results of kinetic studies of the direct synthesis which give evidence for the chemisorption mechanism, and of the side reactions taking place

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in the direct syntheses which lead to silicon containing and silicon free products, which can all satisfactorily be explained by reactions of groups adsorbed on the surface of the contact mass. In this lecture I should like to acquaint you with the results obtained by us over the last three years and show how these results complement or support our earlier conclusion.

In our study of the direct synthesis of arylhalogenosilanes we were interested in how the substituents on the benzene nucleus influence the course of the synthesis. We used in this investigation aromatic bromides because of their lower reaction temperature and because less side-products are produced by these compounds.

For comparing the effect of the structure of aryl bromides on the reactivity, we studied in an integral flow-reactor at 390° the kinetics of the reaction of bromobenzene and individual isomeric bromotoluenes with silicon, using copper as a catalyst. As a measure of the reactivity of these aryl bromides we employed the values of the initial reaction rates of formation of individual products. *Figure 1* shows the time dependence of the composition of the condensed products for the synthesis of *p*-tolylbromosilanes. From these dependences we took the values of the contents of individual products under steady-state conditions, and from them we calculated the conversion of the



*Figure 1.* Time dependence of the composition of the condensate in the direct synthesis of *p*-tolylbromosilanes. Temperature 390°; space velocity of *p*-bromotoluene  $F/W = 5.40$  mol/h kg contact mass original aryl bromide to different products.

From a mass balance established for dependence on temperature it was found that, as expected by analogy with the synthesis of phenylbromosilanes, the main reaction products of bromotoluenes are ditolyl dibromosilane and tolyl tribromosilane; in small amounts toluene and ditolyl are also formed.

In the temperature range 330 to 360° *o*-bromotoluene was less reactive than bromobenzene; the reactivity of the *meta* and *para* isomer was practically the same as that of bromobenzene. At 390° bromobenzene was the most reactive, the conversion of all bromotoluene being practically the same but less than that of bromobenzene.

In order to be able to interpret the kinetic study of the effect of the methyl group bonded to the benzene nucleus on the reactivity of aryl bromides it was necessary to eliminate thermal decomposition of the starting materials and isomerization of bromotoluenes and of the resulting tolylbromosilanes on the contact mass which has the nature of a weak Lewis acid. We have established experimentally that under the reaction conditions studied neither thermal decomposition nor isomerization of the reactants or products occurs.

The initial reaction rates of formation of individual products, from which we calculated the reactivity of aryl bromides, were determined from the dependence of the conversion of the original aryl bromide on the reciprocal space velocity. The conversion of aryl bromide is defined as the fraction of the bromide (moles) reacted to the respective product (moles), and the space velocity is defined as the ratio of the rate of feed of aryl bromide (moles per hour) and the weight of the contact mass (kg). The initial reaction rate of formation of the respective reaction product (moles per hour—per kg of contact mass) equals the slope of the tangent to the initial point of the dependence of the conversion on the reciprocal space velocity. The overall initial rate was calculated as the sum of initial rates of formation of the individual products.

From the kinetic study it followed that the presence of the methyl group on the benzene nucleus leads to a decrease in the overall reactivity of aryl bromides. The reactivity decreases in the order *m*-bromotoluene > *p*-bromotoluene > *o*-bromotoluene. The selectivity is highest in the synthesis of *p*-tolylbromosilane in which the ratio of diaryldibromosilane to aryltribromosilane amounts to 3:1. The least selective is the synthesis of *m*-tolylbromosilanes in which the above ratio is only 1:4 (Table 2). On the whole it may be claimed that the reactivity of individual isomeric bromotoluenes is not much influenced by electronic effects. This, however, may be due to the relatively high reaction temperature. Some significance can be attributed only to the steric effect of the methyl group in the *ortho* position to the bromine atom.

Contribution to $r_{total}$	Bromobenzene	<i>o</i> -Bromotoluene	<i>m</i> -Bromotoluene	<i>p</i> -Bromotoluene
Ar <sub>2</sub> SiBr <sub>2</sub>	57.0	60.0	53.0	69.0
ArSiBr <sub>3</sub>	33.0	27.0	38.0	23.0
ArH	4.0	10.0	7.0	5.0
Ar <sub>2</sub>	6.0	3.0	2.0	3.0
Ar <sub>2</sub> SiBr <sub>2</sub> + ArSiBr <sub>3</sub>	90.0	87.0	91.0	92.0

Table 2. Direct synthesis of phenyl- and tolylbromosilanes at 390°; initial reaction rates  $r_{total}$  (mol/h kg contact mass) bromobenzene 4.9, *o*-bromotoluene 3.0, *m*-bromotoluene 4.0, *p*-bromotoluene 3.6

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Since, with the exception of this *ortho* effect, no other influence of the position of the substituents on the benzene nucleus could be determined under conditions of the direct synthesis, we proceeded to study the reaction kinetics of the series of *para*-substituted bromobenzenes (*p*-Br, C<sub>6</sub>H<sub>4</sub>X, where X = H, CH<sub>3</sub>, *i*-C<sub>3</sub>H<sub>7</sub>, *tert.* C<sub>4</sub>H<sub>9</sub>, F and Cl.) The initial reaction rates of the two parallel reactions were determined in the same manner as for the tolylbromosilanes. For the final comparison of reactivities of the aryl bromides investigated we calculated the relative reaction rates defined as the ratio of initial reaction rates of the respective aryl bromide and of bromobenzene under the same reaction conditions ( $p = 0.97$  atm,  $t = 411^\circ$ )

Table 3. Initial reaction rate  $r^\circ$  and relative initial reaction rate  $r^\circ_{\text{rel}}$  of formation of (XC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiBr<sub>2</sub> ( $r_2^\circ$ ) and XC<sub>6</sub>H<sub>4</sub>SiBr<sub>3</sub> ( $r_3^\circ$ )

X	<i>p</i> -Cl	H	<i>p</i> -F	<i>p</i> -CH <sub>3</sub>	<i>p</i> - <i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>p</i> - <i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>m</i> -CH <sub>3</sub>
$r_0^3$		1.30	1.05	1.00	0.90	0.97	1.52
$r_0^2$		2.45	2.20	1.90	1.60	1.40	2.12
$r_0^2 + r_0^3$	4.85	3.75	3.25	2.90	2.50	2.37	3.64
$r_{\text{rel}}$	1.29	1	0.87	0.77	0.67	0.63	0.83
	+ 0.227	0	+ 0.062	- 0.170	- 0.151	- 0.197	- 0.065

(Table 3). For *p*-chlorobromobenzene the initial reaction rate was determined indirectly from the overall conversion of the aryl bromide, because at higher conversions there probably also take place competitive reactions leading to the formation of chlorosilanes (in addition to chlorobenzene we also determined bromobenzene chromatographically).

By plotting the values of  $\log r^\circ_{\text{rel}}$  against Hammett's constant,  $\sigma$ , we obtained a linear dependence, the correlation coefficient amounting to 0.93 (Figure 2). The slope of the straight line, determined by the method of least squares, was  $\rho = 0.63$ .

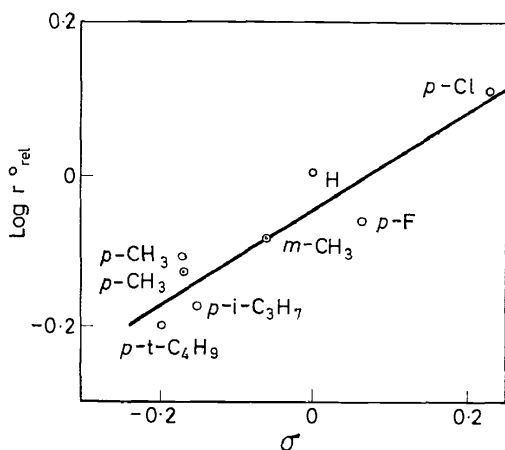


Figure 2. Correlation of  $\log r^\circ_{\text{rel}}$  and Hammett  $\sigma$  constant for reaction of *p*-X C<sub>6</sub>H<sub>4</sub>Br with silicon

The rather large deviation of the initial reaction rate of *p*-fluorophenyl-

bromobenzene from those of the remaining aryl bromides correlated prompted us to study the kinetics of this reaction in greater detail.

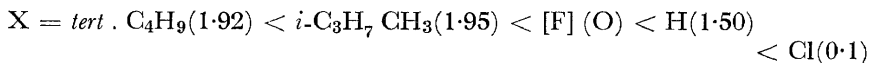
It should be noted, however, that the above mentioned correlation is not quite exact, because we correlated reaction rates which are not a unique measure of the reactivity—their value is influenced also by the adsorption ability of the substance concerned. The most reliable procedure is to determine the effect of structure on reactivity on the basis of the values of rate constants. However, in order to determine these constants we have to know the form of the rate equation, and consequently also the course of the surface reaction.

For these reasons we studied the reaction of *p*-fluorobromobenzene with silicon, catalyzed by copper, as a heterogeneous catalytic reaction in which, firstly, *p*-fluorobromobenzene is adsorbed on the surface of the contact mass, then the surface reaction of the adsorbed bromide with silicon takes place with the formation of *p*-fluorophenylbromosilanes, and finally these products are desorbed. Separately we evaluated parallel reactions in which diaryldibromosilane and aryltribromosilane are formed. From the dependence of the initial reaction rate on the partial pressure of aryl bromide it followed that the rate determining step of this system of reactions is the surface reaction of the aryl bromide with the contact mass; adsorption and desorption proceed under practically equilibrium conditions. (If adsorption were the rate determining step, the reaction rate would be a linear function of the partial pressure. On the other hand, if desorption were the rate determining step, the reaction rate would be independent of the partial pressure). We proposed for this reaction several mechanisms based on the concepts of Langmuir and Hinshelwood, and derived rate equations for these mechanisms. On the basis of the dependence of the initial reaction rate on the partial pressure we chose those mechanisms which corresponded to this dependence. The equations for these mechanisms were linearised, and graphically we determined the rate constants and the adsorption coefficients. Several kinetic mechanisms satisfied the experimental results. To decide between these mechanisms we proceeded in the following manner: from the rate constants and adsorption coefficients we calculated on the basis of temperature dependences the activation energies and standard changes of enthalpy of adsorption of *p*-fluorobromobenzene. In this way we eliminated, for example, the mechanism for which the standard enthalpy changes differed widely from the heat of vaporization of *p*-fluorobromobenzene. The most probable appears to be the mechanism in which two molecules of *p*-fluorobromobenzene adsorbed with dissociation take part in the formation of a molecule of di-*p*-fluorophenyldibromosilane.

Electronic effects of the substituents on the benzene nucleus of the aryl halides can play a role only in the rate determining step—in the surface reaction.

Proposals previously made to explain the higher reactivity or reduced reaction temperature by the increasing polarity or polarizability of the C-halogen bond in the organic halide are satisfactory only for series of aliphatic compounds. The slight differences determined in reactivities of *o*-, *m*- and *p*-bromotoluenes with silicon are in disagreement with the considerable differences in the polarity of these substances ( $\mu$  in benzene: 1.45; 1.77;

1.95). A comparison of the reactivities of individual *p*-substituted bromobenzenes with the corresponding dipole moments reveals that here also the values of  $\mu$  do not correspond to the order of reactivities determined by us for:



In view of the dipole moments of *p*-fluoro and *p*-chlorobromobenzene the reactions of these aryl bromides with silicon would have to be markedly slower than the reactions of bromobenzene and *p*-alkylbromobenzenes. On the other hand, if, as we assumed, the original reactant is, in the direct synthesis of organohalogenosilanes, adsorbed dissociatively on the contact mass, then we can consider the effect of the dipole moment of these compound on their reactivity as insignificant, because the rate determining step is a surface reaction of the adsorbed groups.

On the basis of our results it appears that the probable mechanism of the direct synthesis of arylbromosilanes is one in which the rate determining step is a nucleophilic attack of the silicon atom by bromine, which is accelerated by electronegative substituents on the aromatic nucleus of the organic groups. The formation of aryltribromosilanes can be explained in a similar manner and is probably due to an insufficiency of organic groups which reacted with other substances *e.g.* organobromosilanes to give polyphenylenes; in this case the electronic effects of the organic groups are less pronounced (to one aryl group correspond 3 atoms of bromine), as has also been established by our results (see *Table 3*).

In order to obtain a clearer picture of the important step of the direct synthesis of arylhalogenosilanes—of the adsorption of the organic halide on the contact mass—and to elucidate the nature of the forces acting in this process, we studied by pulse chromatography the sorption of bromobenzene on silicon and copper, and of benzene, toluene, chlorobenzene, bromobenzene, different bromotoluenes, *p*-fluorobromobenzene and *p*-ethylbromobenzene on a mixture of silicon and copper in the temperature range 150 to 210°. The sorption measurements were carried out in a commercial gas chromatograph with thermal conductivity detection; as the carrier gas we used nitrogen and argon.

For calculating for the substances studied their specific adsorption capacity ( $K_A L$ ) on silicon, copper and the contact mass, we used a simple relation derived in our laboratories:

$$K_A L = (t_{rA} - t_{rI}) F_B / SP = t_r F_B / SP$$

- where  $K_A$  is the adsorption coefficient of substance A ( $\text{atm}^{-1}$ ),  
 $L$  is the total number of active sites per unit surface area of the sorbent ( $\text{mol}/\text{m}^2$ ),  
 $K_A L$  is the specific adsorption capacity of substance A ( $\text{mol}/\text{m}^2 \text{ atm}$ ),  
 $t_{rA}$  is the retention time of substance A measured at peak maximum in the chromatogram (min),  
 $t_{rI}$  is the retention time of the unadsorbed inert component as measured from the maximum of its elution peak in the chromatogram (min),

- $F_B$  is the flow rate of the carrier gas (mol/min.),  
 $S$  is the total surface of the sorbent in the column (m<sup>2</sup>)  
 $P$  is the total pressure in the column (atm); it was determined as the arithmetical mean of the pressures at the entrance to and exit from the column ( $P = (P_1 + P_0)/2$ )

The equation was derived for the case of a linear relation between the amount adsorbed and the concentration of the adsorbate in the gaseous phase; according to this the value of  $\Delta t_r$  is independent of the amount of adsorbate injected. We have found, however, that  $\Delta t_r$  is constant only at

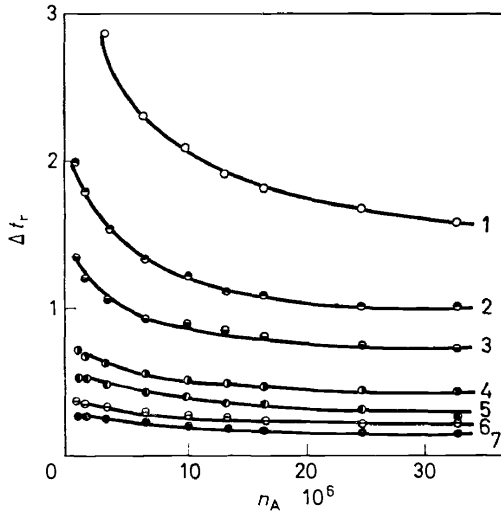


Figure 3. Plot of  $\Delta t_r$  for *m*-bromotoluene against sample size ( $n_A$ ) at various temperatures

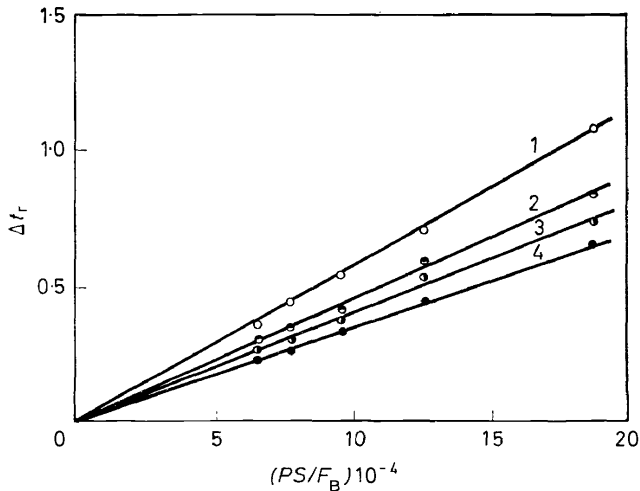


Figure 4. Plot of  $\Delta t_r$  of *o*-bromotoluene against  $SP/F_B$  at various amounts of sample injected at 190°

higher temperatures and for larger samples injected (see Figure 3). The figure

represents a plot of  $\Delta t_r$  from *m*-bromotoluene against sample size at different temperatures; curve 1 is for 149°, 2 for 161°, 3 for 168°, 4 for 180°, 5 for 190°, 6 for 200° and 7 for 210°; contact mass sorbent (35.2 g),  $F_B = 40.56$  mole/min. In the large majority of cases we obtained linear dependencies of  $\Delta t_r$  on  $SP/F_B$  (Figure 4). In this figure are shown plots of  $\Delta t_r$  for *o*-bromotoluene against  $SP/F_B$  for different sizes of the sample injected at 190°; the sample sizes are in moles multiplied by  $10^6$ : curve 1 is for 6.64, 2 for 6.656, 3 for 13.312 and 4 for 33.264; the sorbent was in this case the contact mass. From these dependences we calculated the specific adsorption capacities as slopes of the straight line shown in Figure 3. The heats of adsorption

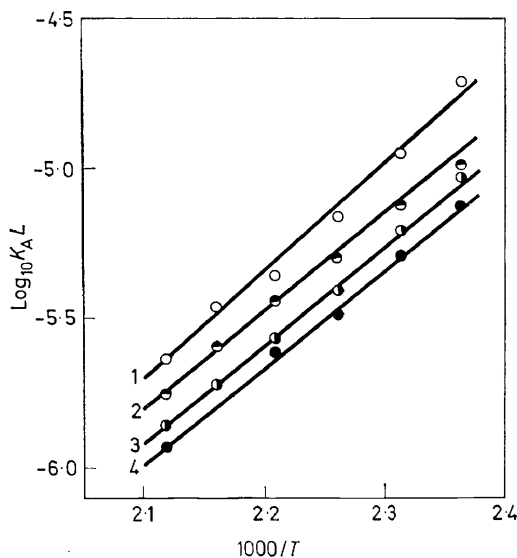


Figure 5. Plot of  $\log K_{AL}$  as calculated from chromatographic data against  $1/T$  at various amounts of bromobenzene injected

of the adsorbates ( $-\Delta H_a$ ) on different sorbents were determined from plots of  $\log K_{AL}$  against  $1/T$  (Figure 5). The curve represents plots of  $\log K_{AL}$  as calculated from chromatographic data against  $1/T$  for various amounts of bromobenzene injected; sample sizes are given in moles multiplied by  $10^6$ : curve 1 is for 1.904, 2 for 7.616, 3 for 15.332 and 4 for 38.090; sorption on the contact mass. The slopes of these dependences decrease with the increasing size of sample injected, which is apparently associated with the increasing coverage of the surface by the sorbent as the amount injected increases.

From the magnitude of the heat of adsorption (see Table 4) of bromobenzene it may be concluded that between bromobenzene and copper a stronger bond is formed than between bromobenzene and silicon. The specific adsorption capacity of bromobenzene on copper was also higher than that on silicon; the value of this quantity for a contact mass which is a mechanical mixture of silicon and copper was between those for copper and silicon.

Table 4. Specific adsorption capacities ( $K_A L \times 10^6$ , mol/m<sup>2</sup> atm) at 170° and heat of adsorption  $\Delta H_a$  (Kcal/mol) of bromobenzene

	$n_A \cdot 10^6$ mol	Si	Cu	Contact mass
Adsorption capacities	5.0	4.9	6.7	5.4
	30.0	3.0	3.4	2.4
Heats of adsorption	5.0	12.8	15.0	15.4
	30.0	12.2	14.0	14.9

In order to simulate as well as possible the conditions of the direct synthesis, we also made orientational measurements of the sorption of bromobenzene and all bromotoluenes on a pre-reacted contact mass. The extent of adsorption was higher than on a mixture of powdered silicon and copper, about 16 times for bromobenzene and 12–13 times for the bromotoluenes. Since the increase in the adsorptivity of the pre-reacted contact mass very much exceeded the gain in its surface area (which increased approximately by a factor of 2) it may be concluded that a considerable number of new active sites are formed in the course of the synthesis.

From the magnitudes of the heats of adsorption of the different adsorbates it is apparent that we do not have here a case of non-specific physical adsorption: the heats of adsorption determined were in all cases higher than the mean heat of condensation over the temperature interval studied (see Table 5).

Table 5. Heats of condensation and heats of adsorption  $\Delta H_a$  (Kcal/mol) of adsorbate on contact mass (Si:Cu = 7:3)

	Benzene	Toluene	Chloro- benzene	Bromo- benzene	Bromotoluene			<i>p</i> -Fluoro- bromo- benzene	<i>p</i> -Ethyl- bromo- benzene
					<i>o</i> -	<i>m</i> -	<i>p</i> -		
Heats of condensa- tion	7.2	7.4	8.4	9.0	10.6	10.1	10.1	—	11.2
Heats of adsorption	10.9	12.0	12.3	15.1	14.8	14.7	14.0	13.1	13.9

All these results lead to the conclusion that this is a case of orientated sorption of arylbromides. The fact that approximately the same heats of adsorption were determined for all the aryl bromides studied indicated that all of them form the same kind of bond, namely a bond between the bromine atom and the surface of the contact mass by means of the electrons of bromine. This is also born out by the fact that electropositive substituents on the benzene nucleus in a *para*-position to the bromine atom aid the formation of this bond whereas electronegative substituents weaken this tendency.

The values obtained for relative adsorption capacities of bromobenzene, *m*-bromotoluene, *p*-bromotoluene, *p*-fluorobromobenzene and *p*-ethylbromobenzene satisfy Hammett's relation:

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$$\log K_A L_{\text{rel}} = \rho \sigma \quad (\text{see Figure 6}).$$

This means that the formation of the bond between bromine and the contact surface is influenced by the inductive effect of the respective groups.

For the injection of  $2.5 \times 10^{-6}$  mole we obtained at  $170^\circ$  a straight line with a value for the correlation coefficient equal to 0.98. As the temperature and size of the sample injected were successively increased, poorer correlations were obtained. Since under the conditions studied by us adsorption was in all cases reversible, we may conclude that electropositive substituents on the nucleus only weaken the bond between aromatic carbon and bromine. At temperatures exceeding  $350^\circ$ , at which a reaction takes place between the aryl halide and the surface of the contact mass, it appears that adsorption is accompanied by a complete cleavage of the bond between aromatic carbon and bromine; this has also been found by us in the study of the kinetics of the direct synthesis of arylbromosilanes.

In the case of *o*-bromotoluene, for which we found lower values of the adsorption capacity than for *m*-bromotoluene and *p*-bromotoluene we must

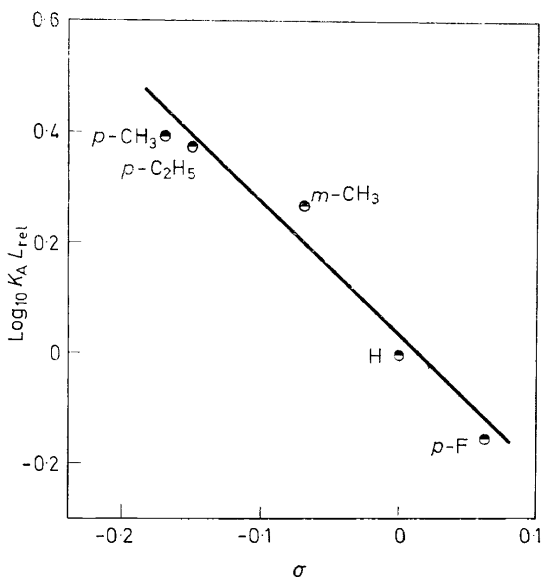


Figure 6. The dependence of relative adsorption capacities  $\log (K_A L)_{\text{rel}}$  of arylbromides  $X-C_6H_4Br$  on Hammett  $\sigma$  constant  
 $443.2^\circ K$ ;  $n_A = 2.5 \times 10^{-6}$  mol contact mass sorbent

apparently take into consideration the steric effect of the methyl group which hinders the formation of a bond between bromine and the contact mass. This is also in agreement with the lowest reactivity of *o*-bromotoluene as determined in our kinetic study. As concerns the order of the compounds benzene, toluene and chlorobenzene, the lowest specific adsorption capacities and heat of adsorption were found for benzene, whereas the adsorption capacities of toluene and chlorobenzene did not differ much from that of bromobenzene. In the case of chlorobenzene we also assume the formation

of a bond between chlorine and the surface of the contact mass, as was the case with bromobenzene.

Insufficient understanding of how different elements, denoted as promoters or inhibitors, affect the course of the direct synthesis of methylchlorosilanes has recently led some authors to propose the hypothesis that the activity and selectivity of the contact mass is associated with the semiconductor properties of silicon. In our Institute we therefore studied the reactivity of n- and p-type silicon in the synthesis of methylchlorosilanes. These kinds of silicon are obtained by doping, with elements of groups V and III, high-purity silicon prepared by zone refining. The doping elements can replace a silicon atom in the crystal lattice. For example, if a silicon atom in the lattice is replaced by an atom of phosphorus then four of the five valence electrons of phosphorus form covalent bonds with the neighbouring silicon atoms; the fifth electron is transferred to an adjacent silicon atom, and by the effect of the applied electric field this electron moves successively from one silicon atom to the next towards the crystal surface. The semiconductivity resulting from this is known as n-type, and the doping elements is termed a donor. Group III elements have a different effect.

Table 6. Direct synthesis of methylchlorosilanes with semiconducting silicon

Added element	Concentration atom . cm <sup>-3</sup> Si	Temperature °C	Reaction time	Product g	Dimethyl-dichlorosilane % w.
—	—	370	40	101.9	46.3
P	10 <sup>19</sup>	350	42	115.7	65.7
O	10 <sup>18</sup>	400	14	19.5	20.1
B	10 <sup>19</sup>	420	12	11.6	22.3
Al	1.27 × 10 <sup>17</sup>	370	30	98.5	52.4
Al	0.9 × 10 <sup>18</sup>	360	32	105.7	58.6
Al	1.63 × 10 <sup>19</sup>	350	30	123.5	68.4
Al	10 <sup>20</sup>	300	26	147.3	76.6
Al	10 <sup>20</sup>	280	28	133.2	85.7

For example, boron introduces into the lattice only three valence electrons which form with the neighbouring silicon atoms covalent bonds. In the fourth bond one electron is missing and this produces an electron "hole" which is attracted towards the neighbouring atom of silicon, and because of the electric field the defect moves successively towards the crystal surface. This is known as p-type semiconductivity and the doping element is an acceptor.

Aluminium-containing p-type silicon reacted already at 280° and the reaction product contained 85 per cent dimethyldichlorosilane (see Table 6). On the other hand, the lowest reaction temperature of n-type silicon containing phosphorus was 350° and the reaction mixture contained only 65 per cent dimethyldichlorosilane.

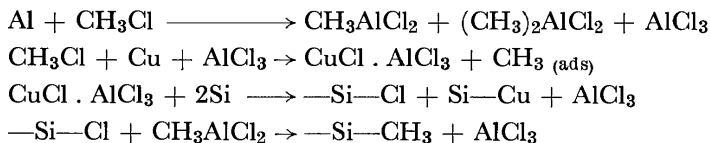
Silicon prepared by zone melting in the presence of air, which has oxygen incorporated into the lattice, was even less reactive; this silicon is also n-type. The reaction proceeded only when the temperature was raised to 400°, and the reaction product contained only 20 per cent dimethyldichlorosilane.

However, after carrying out an experiment with p-type silicon containing boron and finding that the reaction was incomplete even at 420° it became clear that the reactivity of silicon cannot be correlated with its semiconductive properties, and that the explanation of these results has to be looked for elsewhere.

Since we obtained the best results with silicon containing aluminium, we decided to study the reaction with semiconducting silicon containing aluminium in various concentrations ( $10^{17}$ – $10^{18}$  atoms of aluminium per cc of silicon) and with technical grade silicon containing only 0.015 per cent of aluminium which was subsequently alloyed with 0.05, 0.4 and 0.8 per cent of aluminium, respectively. It was found that an admixture of aluminium decreases the reaction temperature. A substantial decrease from 370° ( $10^{17}$  atoms of aluminium) to 280–300° occurs only when the concentration of aluminium is increased to  $10^{20}$  and more. This relatively high concentration of aluminium also speaks against the idea that the reactivity of silicon depends on its semiconductivity.

It is known that aluminium in small amounts forms with silicon substituted solutions. At higher concentrations aluminium is deposited in dislocations, and at still higher concentrations it forms with silicon an eutectic mixture. Aluminium can react with oxygen contained in silicon to form Al—O, A—O—Al structures, or  $AlO_4$  tetrahedrons or their aggregates.

Aluminium, which in the reaction with methyl chloride is much more reactive than silicon, initiates the reaction with the formation of methyl aluminium chlorides.



Aluminium chloride formed by this reaction aids the reaction between methyl chloride and copper, and also catalyses the reduction of cuprous chloride by silicon. This reduction can be considered as the initial step of the regular course of direct synthesis. It may be assumed that in addition to this methyl aluminium chloride reacts with the Si—Cl bond.

Like aluminium, other elements can also be incorporated into the silicon lattice or be deposited in dislocations of silicon crystals; these elements, depending on their ability to react with methyl chloride, can influence the direct synthesis positively or negatively. It is known, for example, that boron does not react readily with methyl chloride to form boron trichloride, the temperature of reacting being 600°. Therefore even small amounts of boron strongly de-activate silicon in its reaction with methyl chloride. Phosphorus, on the other hand, reacts with methyl chloride even at 350°, and silicon containing phosphorus also reacted at this temperature. We can therefore discuss the effect of certain admixtures as activators or inhibitors of the catalytic process.

With technical grade silicon, which always contains several admixtures, the situation is even more complex. It is very probable that in this case

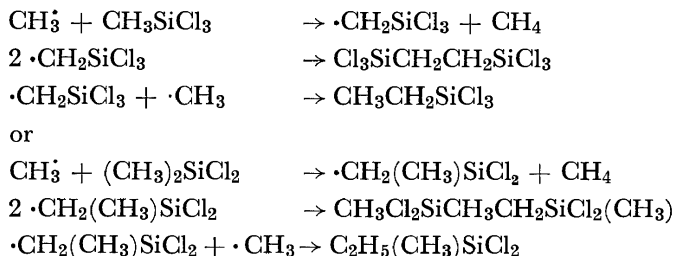
competitive occupation of the dislocations occurs, and the resultant reactivity of silicon will be influenced by the mutual ratio of different elements deposited in the dislocations. Furthermore, when the concentration of the admixtures is higher they are deposited in the interstices between the silicon grains which become coated by them.

In connection with the free-radical theory of the direct synthesis of methylchlorosilanes, we were interested in the reaction of free methyl radicals with some methylchlorosilanes in the gaseous phase. The kinetics of this reaction have been studied by Kerr, Slater and Young who prepared the free methyl radicals by photolysis of azomethane in the presence of chlorosilanes. They expressed their results by means of parameters of the Arrhenius equation, for the following reactions:

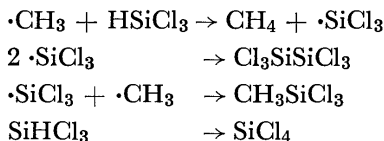
	E kcal.mol <sup>-1</sup>	log A mol <sup>-1</sup> cc.sec <sup>-1</sup>
$\text{CH}_3\cdot + \text{SiHCl}_3 \rightarrow \text{CH}_4 + \cdot\text{SiCl}_3$	8.5	13.4
$\text{CH}_3\cdot + \text{CH}_3\text{SiCl}_2 \rightarrow \text{CH}_4 + \cdot\text{CH}_2\text{SiCl}_2$	11.5	12.9
$\text{CH}_3\cdot + \text{CH}_3\text{SiHCl}_2 \rightarrow \text{CH}_4 + \text{CH}_3\dot{\text{S}}\text{iCl}_2$	7.2	11.6
$\text{CH}_3\cdot + (\text{CH}_3)_2\text{SiCl}_2 \rightarrow \text{CH}_4 + \text{CH}_3(\dot{\text{C}}\text{H}_2)\text{SiCl}_2$	11.6	13.2

The above named authors have found that the Si—H bond reacts with free methyl radicals. They did not separate the reaction products, and followed the course of the reaction by determining the contents of methane, ethane and nitrogen.

For our work we prepared the silane compounds formed in the reactions of free methyl radicals with methylchlorosilanes by pyrolysis of dimethylmercury at 420° in the presence of methyltrichlorosilane, dimethyldichlorosilane, trichlorosilane and methyldichlorosilane. On identifying the main products formed in these reactions we have found that, as expected, their formation can be explained by the recombination of free radicals, as for example:

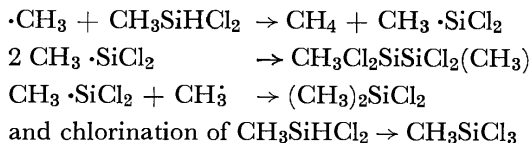


With chlorosilanes containing the Si—H bond, the replacement by chlorine of hydrogen bonded to silicon also takes place:



However the chlorination of trichlorosilane is not clear. It can not be explained by the disproportionation of trichlorosilane, because in a compara-

tive experiment involving only trichlorosilane, without dimethylmercury, we found only a slight amount of tetrachlorosilane. The formation of substantial amounts of tetrachlorosilane in the reaction of trichlorosilane with dimethylmercury is probably associated with the formation of methylchloromercury, which has been separated from the products of the reaction with methyltrichlorosilane and dimethyldichlorosilane, but has not been found in the analogous products of trichlorosilane and methyldichlorosilane. It appears that in the last named cases it was consumed for chlorination of the Si—H bond. The higher reactivity of the Si—H bond with free methyl radicals than that of the C—H bond is also clearly evident from the composition of the products in the reaction of dimethylmercury with methyldichlorosilane where, for the major part, only the Si—H bond reacts:



and from the fact that in the reaction with trichlorosilane and methyldichlorosilane the conversion of methyl radicals amounts to 60–70 per cent whereas the analogous conversion of methyltrichlorosilane and dimethyldichlorosilane is only 15–20 per cent. The complement to 100 per cent is due either to the mutual reaction of free methyl radicals or to their thermal decomposition.

By gas chromatography we have found that in addition to the above named compounds there are in all cases three or four other substances also formed. They are present in very small amounts and they have not been identified.

The products which we have obtained and identified have also been separated from the higher boiling fractions after distilling off methylchlorosilanes. In this respect the results obtained are not in disagreement with the free radical theory of the direct synthesis of methylchlorosilanes. However, in disagreement with this theory is our finding that the Si—H bond preferentially reacts with free methyl radicals, which would exclude the formation of trichlorosilane and methyldichlorosilane. This fact is especially manifested in the direct synthesis of ethylchlorosilanes where we obtained as much as 40–50 per cent ethyldichlorosilane, and from the distillation bottoms we separated the compound pentachlorodisilethylene,  $\text{HCl}_2\text{SiCH}_2\text{CH}_2\text{SiCl}_3$ . On the basis of these findings and of our previous results, as well as results of other authors, we believe that the majority of reactions in direct synthesis take place on the surface of the contact mass and that direct synthesis can be considered to be a catalytic heterogeneous reaction.

I cannot avoid concluding my lecture on a rather sceptical note. I believe that the present state of science does not allow a detailed explanation of the reaction mechanism of so complex a chemical reaction as the direct synthesis of organohalogenosilanes. Kinetic studies and physical measurements can provide only indirect proofs, and information going beyond this would probably require an effort out of all proportion to the practical value of the results obtained. For this reason we are winding up our chemical research on direct syntheses and in the future we shall concentrate our attention on

chemical engineering research topics which, we hope, will give important results for improving the design of the reactor for these syntheses and mastering their manufacture on an industrial scale.

I would like to state my opinion that the present state of knowledge indicates quite convincingly that for the direct synthesis of organohalogenosilanes the chemisorption mechanism is of decisive importance, without, however, excluding the possibility that under such high reaction temperatures the radical mechanism may also have a minor effect.

*In conclusion I would like to acquaint you with the names of my colleagues who worked on our contribution in this field: J. Joklík, F. Jošt, M. Kraus, O. Kruchňa, J. Rathouský, L. Scháněl, K. Setínek, and M. Varuška.*