

Mechanism and Kinetics of the Metal-Catalyzed Synthesis of Methylchlorosilanes

IV. The Mechanism of the Synthesis of Dimethyldichlorosilane from Silicon and Methyl Chloride

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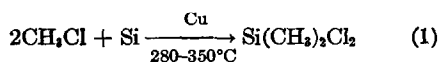
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The aim of the present investigation is to improve our knowledge of the mechanism. The radical mechanism proposed by Hurd and Rochow is rejected in favor of an ionic mechanism. To verify the influence of the polarity of the solid surface on the selectivity of the reaction, the catalytic behavior of some polar and nonpolar metal silicides in their reaction with methyl chloride have been investigated. Heats and entropies of adsorption of methyl chloride and methyl bromide on silicon-copper are calculated, using a model based on the ionic mechanism. The rate-determining step of the reaction is discussed with regards to published kinetic data.

1. INTRODUCTION

Silicones are produced by hydrolysis of organochlorosilanes and subsequent polycondensation of the so-formed organosilanol. The most important type of silicones used at present are the methyl silicones. As for the production of silicone oils and rubbers difunctional monomers are required, which are likely to form linear polymeric chains, it is of interest to dispose of a specific manufacturing method for dimethyldichlorosilane. Such a method was introduced by Rochow (1) and Müller (2, 3) who applied copper as a catalyst for the direct action of methyl chloride on silicon [Reaction (1)].



Other organohalides often react similarly (4). It is possible to obtain a mixture of methylchlorosilanes with at best about 80% to 90% of dimethyldichlorosilane (5-9). Other catalysts have been used as well, leading to the formation of other methylchlorosilanes as main products (10).

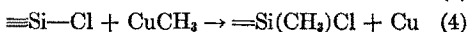
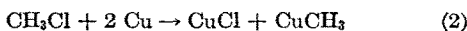
The selectivity of the process [Reaction (1)] has been shown to be strongly dependent on the actual form of the copper catalyst. Considerable chemical, microscopic, and röntgenographic evidence made it clear that not merely copper, but an alloy of silicon and copper is the real catalyst (8, 11). The η phase and the ϵ phase of the binary system copper-silicon (12) were studied in this respect (11b). Copper as such catalyzes side reactions and as a consequence the selectivity of the process can be improved by the removal of free copper (8, 9).

Proposed Mechanisms

The mechanism of the reaction of copper-silicon with organohalides was studied by Rochow and Hurd (13), Trambouze (14), Klebansky and Fikhtengolts (15, 16), Bažant *et al.* (17-19) and Vlugter and Voorhoeve (7).

Rochow and Hurd (13) consider the reaction to be of a free-radical type between intermediate products formed by splitting the methyl chloride with copper in the

neighborhood of silicon. The course of the process according to those authors is depicted in Reactions (2-4).



Reactions similar to (3) or (4) may proceed until the four silicon valencies are saturated and volatile methylchlorosilanes are formed. Selective synthesis of dimethyldichlorosilane is inadequately explained by the above hypothesis. The following objections hold against the proposed mechanism.

1. The reaction of organochlorides with silicon is possible far below the initiation temperature for the reaction of copper(I) chloride and silicon (20).

2. Tetramethylsilane is one of the reaction products. This is not in accordance with a mechanism where the initial chlorination of the silicon is considered to be essential.

3. The proposed mechanism would predict an at random distribution of the various methylchlorosilanes. This is in conflict with the observed pronounced selectivity towards dimethyldichlorosilane.

4. It is not a necessary consequence of this mechanism that the copper must be present as an intermetallic compound with silicon to yield selectively dimethyldichlorosilane.

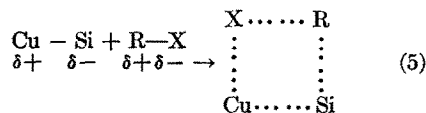
5. At 300° to 350°C the decomposition of methyl chloride on copper is much slower than the formation of silanes.

6. The reaction of copper(I) chloride with silicon occurs so rapidly under the prevailing conditions for the synthesis that a high amount of silicon tetrachloride and other chlorine-rich substances would be expected in the reaction product.

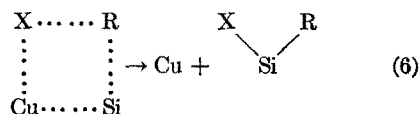
Especially at lower temperatures the composition of the obtained products deviates considerably from that expected by the Rochow-Hurd mechanism.

A more satisfactory explanation of the selective formation of diorganodihalogenosilanes is given by Klebansky and Fikhtengolts (15, 16) and by Trambouze (14) by assuming a dissociative adsorption of

methyl chloride on the partially ionic surface of a copper-silicon alloy. The orientation of the methyl chloride on the surface is controlled by its dipole momentum and by the charge partition between copper and silicon. According to Klebansky and Fikhtengolts the methyl group is being attached to silicon and the chlorine to copper in this adsorption. This is schematically illustrated by (5).

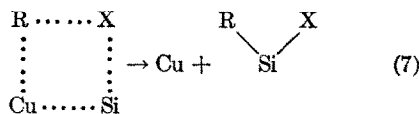


The subsequent step is an electron shift in the adsorbed complex [Reaction (6)].



Both products of the latter reaction are still attached to the silicon-copper lattice. In this scheme the methyl and chlorine are always in the direct vicinity of the reacting silicon atom and so a selective formation of a molecule with an equal number of methyl and chlorine groups is plausible.

Trambouze (14) and Joklík, Kraus, and Bažant (19) assume that the adsorption will occur in the reverse direction, methyl being bound to copper and chlorine to silicon. The next step would be the electrophilic (19) transmission of methyl from copper to silicon [Reaction (7)].



The latter authors argue that the reaction of methyl bromide with silicon-copper is expected to be faster than that of methyl chloride because in the adsorbed complex bromine withdraws electrons from silicon less powerfully than chlorine, which results in a higher rate for Reaction (7). This was indeed observed (19). However, the above interpretation of the kinetic data does not take into account the fact that the discussed electronic effects mainly influence the activation energy. As experimentally a

higher activation energy for the reaction with methyl bromide was found [25.3 kcal/mole for methyl chloride and 37 kcal/mole for methyl bromide (19)], this evidence does not seem to be in line with the proposed explanation.

2. THE CHARGE PARTITION IN METAL SILICIDES

Klebansky and Fikhtengolts (15, 16) claim that the polarity of the surface plays an essential role in the hypothesis for the selectivity. These authors assume that the copper atom is positive, the silicon atom negative. However, nothing is actually known about the charge distribution.

Yet there is some evidence for the proposed distribution. The electronegativities, defined by Pauling (21) as the attractivity of the neutral atom for electrons, yield no very reliable results in the case of metallic compounds. However, the Pauling values for silicon (1.8) and copper (1.9) are derived for distinct compounds. These values have been revised by Sanderson (22) to be 1.74 for silicon and 1.64 for copper. Darken and Gurry (23) stated that for intermetallic compounds and solutions a value of about 1.5 for copper (and silver) would better fit the solubility of many elements in these metals. Pauling (21, p. 432) indicates that in metallic systems copper can be regarded as an element preferably enlarging its valency by electron release ("hypercubic"). Moreover it is known that copper solved in germanium is completely ionized (24).

This collected evidence indicates that the charge distribution assumed by Klebansky and Fikhtengolts may probably be correct. According to these authors, the selectivity of the reaction between organohalides and silicon-copper is controlled by the interaction of the dipoles of the organohalide and the surface during the adsorption step.

To study the consequences of the polarity of silicide surfaces for the reaction with methyl chloride some attention is also given to the behavior of calcium, chromium, and iron. A good deal of attention is paid in the literature to the electronic structure of the silicides of calcium, chromium, and iron.

Here again, the Pauling electronegativities of the elements do not give much information about the charge distribution in the silicides, except when the electronegativity differences are considerable.

Thus, the electronegativity of calcium is 1.0. It is to be expected that calcium bound as a silicide will have a rather large positive charge, by release of its valence electrons to the 3*d* orbitals of silicon. This qualitative approach of the electronic structure of calcium silicides is in accordance with Golutvin's interpretation (25) of their high heat of formation, exhibiting a maximum (when expressed in kcal/g atom) at CaSi. The maximum ionization of the metal atom appears here (and in the case of vanadium and titanium too) in the silicon-richest alloys, as a result of the limited ability of silicon to bind electrons.

The silicides of iron and nickel have been investigated by Golutvin (25), Kolomiets *et al.* (26), Crangle and Martin (27), Nemnonov and Kolobova (28), and Nemnonov, Sorokina, and Menshikov (29). In the metallic state iron and nickel possess the electron configuration $(3s)^2(3p)^6(3d)^{2.3}(4s + p)^{5.7}$ and $(3s)^2(3p)^6(3d)^{9.4}(4s)^{0.6}$, respectively (30). In combination with silicon these metals try to fill their partly empty 3*d* orbital by attracting the valence electrons of silicon. In the case of nickel silicide this has been demonstrated by Nemnonov and Kolobova (28) with the aid of the decrease of the magnetic moment per nickel atom by the introduction of silicon atoms. Crangle and Martin confirm this (27). The lengths of the metal-silicon bonds provide another indication that these silicides have a partially ionic character. Nemnonov, Sorokina, and Menshikov (29) focused attention on the appreciable shortening of the bond lengths in silicides of iron and nickel as compared to the sum of the metallic radii.

Chromium has an intermediate position between the calcium-titanium-vanadium group and the iron-cobalt-nickel group. This is already revealed by the fact that the bond distance between Cr and Si in Cr₃Si is equal to the sum of the atomic radii, implicating a purely covalent bond

(29, 31). The only very slight variation of the gram atomic heat of formation of the chromium silicides with their composition indicates the same (25). The increase in electrical conductivity above 200°C, observed by Nikitin (32, 33) and Robins (34), can also be explained by this covalent character (25).

It is now possible to frame a series of metals which, if bound to silicon, attract or release electrons. In sequence of decreasing positive charge or increasing negative charge on the metal atom this series becomes: Ca, Ti, Cu, Cr, Fe, Ni. Some members of this series have been investigated as catalysts in the direct synthesis.

3. EXPERIMENTAL METHODS

The reaction of methyl chloride with the silicides was carried out in a small, stirred fluid-bed reactor with a capacity of about 8 ml. Full details of the apparatus were published earlier (8, 11b). The effluent from this reactor was led through a gas sampling device, by which samples of it could be introduced directly into a gas chromatograph. By means of this unit it was possible to determine the composition of the products and the conversion of the methyl chloride and consequently the reaction velocity. Of course an absolute calibration of the unit is necessary because of the very low conversions of the methyl chloride. The gas chromatograph used contained nitrobenzene on Chromosorb as a stationary phase (35) and hydrogen, dried by molecular sieves, as a carrier gas.

The methyl chloride used was gas chromatographically pure. The iron alloy had a purity of 98%, the main impurity being oxygen. The chromium alloy was 99% pure, the main impurities being iron (0.4%), aluminum (0.1%), magnesium (0.1%), calcium (0.05%), and oxygen. The alloys were crushed shortly before use and sieved. The fraction between 50 and 210 μm (10^{-6} meter) was applied for the reaction.

4. EXPERIMENTAL RESULTS

The reaction of methyl chloride with calcium silicides, prepared from the melt, with copper as a promoter, has been in-

vestigated by Bluestein (36). To activate the contact mass, hydrogen chloride was added to the methyl chloride. At 300°C and using 5% of hydrogen halide a product was obtained consisting largely of trimethylchlorosilane, with some other methylchlorosilanes. The composition of this product is given in Table 1. From the product com-

TABLE 1
THE REACTION OF METHYL CHLORIDE
WITH CALCIUM SILICIDE

Temp. (°C)	Composition of the product* % (wt)				
	S	M	D	T	DH
300	7.6	61.6	13.1	7.9	4.8

* S stands for tetramethylsilane, M for trimethylchlorosilane, D for dimethyldichlorosilane, T for methyltrichlorosilane, and DH for methyldichlorosilane.

position it is clear that the silicon valencies are mainly saturated by methyl groups, in accordance with the expected strong adsorption of the methyl groups on the silicon atom and of the chlorine on calcium in the very polar calcium silicide.

The reaction of methyl chloride with copper silicides is described by many authors (5-9). Pure silicides have been used especially by Kolster and the present authors (11b). The main product at optimum conditions is dimethyldichlorosilane (90%), accompanied by methyltrichlorosilane and trimethylchlorosilane.

The reaction of methyl chloride with chromium silicide is effected with an alloy containing 20% (wt) of chromium, probably as CrSi_2 . The reaction exhibited an induction period of 1.5 hr at 380°C. The reaction velocity was very low, 0.001 to 0.003 g silane per hr and per g silicon present in the reactor. The composition of the products turns out to be in line with the expectation for a nonpolar silicide without directive influence for a special orientation of adsorption. The high yield of methyldichlorosilane in the products indicates an important contribution of the cracking of methyl chloride.

The results are collected in Table 2.

TABLE 2
THE REACTION OF CHROMIUM SILICIDE
WITH METHYL CHLORIDE^a

Period No.	Product composition % (wt) ^b			Reaction velocity (mg silane/hr)	Temp. (°C)
	D	T	DH		
1	18.2	57.5	24.2	8.6	377
2	19.5	52.0	28.6	8.6	376
3	21.5	50.8	27.5	10.4	379
4	20.3	56.7	23.0	29.3	411
5	24.2	49.2	26.6	30.6	413
6	27.1	59.3	13.7	18.2	401
7	31.6	51.0	17.4	21.1	396
8	34.3	49.2	16.5	17.6	393
9	30.7	45.0	24.4	19.6	393
10	32.1	44.0	24.0	17.5	391

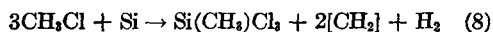
^a The reaction is effected with 11.3 g of the alloy. Methyl chloride flow: 5.3 g/hr. Stirrer: 60 rpm.

^b See footnote, Table 1.

From the measurements in Table 2, the activation energy is estimated by means of an Arrhenius graph. This leads to a value of 31 ± 3 kcal/mole.

The reaction of iron silicide with methyl chloride is studied with an alloy containing 45% (wt) silicon, a composition intermediate between the intermetallic compounds FeSi₂ and FeSi. The reaction exhibited a period of very low activity, lasting for 3 hr at 355°C. Afterwards the reaction velocity is of the order of 0.005 to 0.030 g silane per hr and per g silicon present in the reactor.

The product composition is in accordance with that expected for a silicide with a polar surface with negative iron atoms. The high selectivity is in line with the considerable polarity of the iron silicide. The composition of the product is not very sensitive to temperature. The amount of cracked products, such as methyldichlorosilane and tetrachlorosilane, is remarkably low. The main reaction is probably:



The methylene groups give rise to the formation of coke and hydrocarbons. The results are collected in Table 3. From an Arrhenius graph the activation energy is estimated to be 31 ± 3 kcal/mole.

TABLE 3
THE REACTION OF METHYL CHLORIDE
WITH IRON SILICIDE^a

Period No.	Product composition % (wt) ^b			Reaction velocity (mg silane/hr)	Temp. (°C)
	D	T	M		
1	9.4	86.8	3.9	73	357
2	8.5	88.6	2.8	80	362
3	6.1	91.4	2.5	104	362
4	5.3	92.5	2.2	67	357
5	7.3	91.1	1.6	104	360
6	6.1	92.5	1.5	96	363
7	6.3	91.2	2.3	48	348
8	8.5	89.7	1.7	49	346
9	7.9	91.2	0.9	43	343
10	7.3	91.4	1.3	34	344
11	7.8	91.2	1.0	50	345
12	6.3	92.9	0.8	46	345
13	7.2	91.7	1.1	54	345
14	6.6	92.4	1.0	48	344
15	8.0	91.2	0.8	46	340
16	8.6	91.2	0.8	46	340
17	9.1	90.0	0.9	38	331
18	9.4	89.2	1.5	33	331
19	3.5	84.4	0.4	205	381
20	3.7	86.9	0.1	198	380

^a The reaction was effected with 15.3 g alloy. Methyl chloride flow, 5.3 g/hr. Stirring speed, 60 rpm.

^b See footnote, Table 1.

5. THE CORRELATION OF THE POLARITY OF A SILICIDE SURFACE AND THE SELECTIVITY OF ITS REACTION WITH METHYL CHLORIDE

The composition of the products obtained by the reaction of methyl chloride and a number of silicides appeared to be at least qualitatively dependent on the polarity of the solid surface. The adsorption step is likely to be determinant for the selectivity of the process. The more strongly negative the silicon is in the silicide, the more methyl groups get linked to it during the reaction. From a survey of the results, presented in Table 4, it appears that the place of the copper silicide, as judged from the products of its reaction with methyl chloride, should be between calcium silicide and chromium silicide. This implies a negatively charged silicon atom and a positively charged copper atom, in accordance with the scarce evidence mentioned earlier about the electronic struc-

TABLE 4
THE PRODUCT COMPOSITION VS. THE CHARGE
DISTRIBUTION IN THE SILICIDE

Silicides in order of decreasing positive or increasing negative charge on the metal atom	Charge distribution		Main product*
	Metal	Silicon	
Ca-Si	+	-	M
(Cu-Si)	(+)	(-)	D
Cr-Si	0	0	D + T
Fe-Si	-	+	T

* See footnote, Table 1.

ture of the copper silicide. In our opinion these important findings justify the basic assumption of Klebansky and Fikhtengolts.*

6. THE MECHANISM OF THE SELECTIVE SYNTHESIS OF DIMETHYLDICHLOROSILANE FROM METHYL CHLORIDE AND SILICON-COPPER

The charge distribution in the copper silicide and the direction of the adsorption being established, it now became possible to expand on the basic assumption of Klebansky and Fikhtengolts. In Fig. 1(a) a part of the silicon-copper lattice is depicted. The symbol M denotes an atom of the grid, be it copper or silicon. Two methyl chloride dipoles are physically adsorbed, the direction of the adsorption being determined by the indicated electrostatic interactions. From the state depicted in Fig. 1(a) the system moves to a chemisorbed complex [Fig. 1(b)], with the methyl groups firmly linked to silicon and chlorine linked to copper. The arrows in the latter bonds indicate that the majority of the bonding electrons remains with the chlorine, which consequently is ionic. The adsorbed complex is drawn again in Fig. 2, which gives a view perpendicular to the surface.

* The catalytic action of lead and tin, published earlier (10) cannot be understood along these lines, as these metals do not form intermetallic compounds or solid solutions with silicon. Judged from the temperature of reaction in these cases it seems probable that these reactions proceed by the decomposition of methyl chloride as a first step.

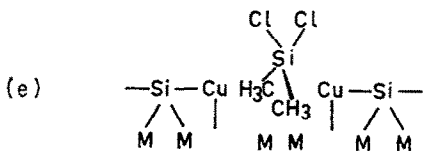
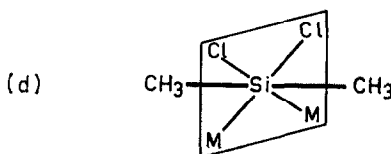
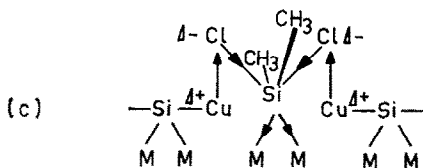
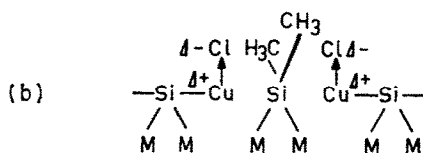
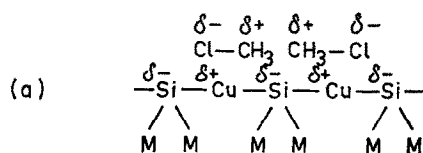


Fig. 1. Steps in the formation of dimethyldichlorosilane: (a) Physical adsorption. (b) The chemisorbed state. (c) Formation of the transition state. (d) The transition state (penta-coordinated silicon is also possible). (e) Adsorbed dimethyldichlorosilane.

In the case of iron silicide the adsorption will occur in the reverse direction. With copper silicide that kind of adsorption perhaps occurs too, prior to the formation of methyltrichlorosilane. For a further

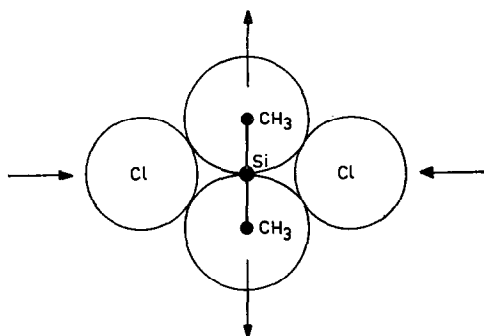
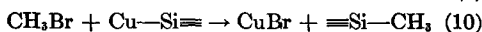
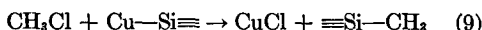


Fig. 2. View on the chemisorbed complex, perpendicular to the surface.

discussion of the mechanism of the formation of side products or of the reactions of methyl chloride with other silicides than that of copper, see ref. (8).

The heat of formation of the chemisorbed complex [Fig. 1(b)] can be calculated, presuming that full bonds are formed. This corresponds to the calculation of the heat of reaction of Reactions (9) and (10), for methyl chloride and methyl bromide, respectively.



As the heat of formation of the silicon compounds is not known, the calculation is carried out with the bond energies, as defined by Pauling (21). Numerical values given by Pauling are used for C-Cl, C-Br, and Si-C. For Cu-Si 46 kcal/mole is used

TABLE 5
COMPARISON OF THE CALCULATED AND
EXPERIMENTAL VALUES FOR THE HEAT
AND THE ENTROPY OF ADSORPTION^a

	Experimental ^b			Calculated	
	MeCl(t)	MeCl(p)	MeBr(p)	MeCl	MeBr
ΔH_A	-21.0	-4.7	-27.4	-23	-28
ΔS_{total}	-48	-18	-49	-54 ^c	-57 ^c
ΔS_{transl}	—	—	—	-41.2	-42.8
ΔS_{rot}	—	—	—	-13	-14

^a The enthalpy unit is kcal/mole, the entropy unit is cal/mole °K.

^b (t) and (p) regard to technical and pure silicon.

^c Calculated as the sum of the rotatory and translatory contributions.

(8) and the values for Cu-Cl (78.5 kcal/mole) and Cu-Br (70.2 kcal/mole) are calculated from Rossini's data (37). The obtained values of the heats of adsorption, together with the experimental values from the work by Bažant *et al.* (18, 19, 38) are collected in Table 5.

The entropy changes accompanying the adsorption are calculated too. With the aid of the formulations given by Fast (39, p. 246) the entropy of rotation and of translation can be calculated for methyl bromide and methyl chloride. It is assumed that chemisorption corresponds to a loss of the translatory and perhaps part of rotatory contributions to the entropy. From kinetic data from Bažant (18, 19, 38) experimental values are calculated by assuming the adsorption constant K_A , can be expressed by

$$K_A = \exp[(\Delta S_A/R) - (\Delta H_A/RT)]$$

These entropy values too are collected in Table 5.

Based on the figures in Table 5 it appears that methyl chloride on technical silicon-copper and methyl bromide on pure silicon-copper are very strongly adsorbed. The heats of adsorption are about equal to the heats of reaction in (9) and (10). The entropies of adsorption indicate that the methyl halides not only lost their entropy of translation, but part of the rotational entropy too. This would be in accordance with a rather rigid structure of the chemisorbed complex (Fig. 2). These results confirm again the assumed adsorption direction. The adsorption of methyl chloride on pure silicon-copper is not strong and approaches physical adsorption. This is in line with the experimental entropy change, which is not much more than one-third of the translational entropy of methyl chloride in the gas phase.

The rate-determining surface reaction is given by the formulations in Fig. 1(c), (d), and (e). In the transition state [Fig. 1(c) and (d)] the 3d orbitals of silicon are likely to play a role. Octahedral sp^3d^2 or bipyramidal sp^3d hybridization of the silicon ligands can take place. In Fig. 1(c) heavy arrows are placed in the reaction

path. In fact this reaction is a nucleophilic substitution of the M ligands by the chlorine ions. In the transition state the M-Si bonds are elongated. The methyl groups are bent on the surface. Figure 1(d) gives a schematic picture of the octahedral transition state. The directions in which the methyl and chlorine groups move during the reaction, as projected on the surface, are given by arrows in Fig. 2.

The strength of the bond formed between the halogen atom and copper has an important impact on the activation energy, as this bond has to be broken prior to reaction. A second factor influencing the energy barrier is the nucleophilicity of the halogen ion. These two factors should cause a high activation energy for methyl bromide, respective to methyl chloride. Experimentally, with pure silicon-copper, an activation energy of 25.3 kcal/mole was found for methyl chloride and of 37.0 kcal/mole for methyl bromide.

The impossibility of the reaction of methyl iodide with silicon-copper (19) and the possibility of the reaction of trifluoromethyl iodide with this silicide (40) lend further support to the mechanism proposed above. Withdrawal of electrons from the silicon in the transition state by the fluorines promotes the reaction, as was expected.

The nucleophilic rate-determining step leads to the expectation that factors increasing the electron density on the silicon atom will decrease the reaction velocity, mainly by influencing the activation energy. Hence the activation energy of the rate-determining step will be increased by substituting methyl by ethyl in the alkyl halide. To study these consequences a further kinetic investigation of the reaction of ethyl chloride with silicon-copper is needed. It has to be emphasized that a dissociation of ethyl chloride to ethylene and hydrogen chloride must be prevented then, possibly by maintaining a high ethylene pressure.

7. CONCLUSIONS

The course of the reaction of methyl chloride with metal silicides has to be considered as being determined by the elec-

trostatic interactions between the methyl chloride dipole and the polar metal-silicon surface. The methyl chloride is dissociatively chemisorbed, the organic group becoming bound to silicon, the chlorine atom to copper. The rate-determining step can be considered as a nucleophilic substitution of the bond between silicon and the metallic crystal lattice by ionic chlorine. The transition state requires an octahedral or bipyramidal hybridization of the silicon orbitals. Kinetic work is in line with the proposed mechanism, which is further supported by published chemical data.

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