JOURNAL OF CATALYSIS **134**, 168–178 (1992)

The Direct Synthesis of Methylchlorosilanes

I. Steady-State and Transient Reaction Kinetics

JONG PAL KIM AND DAVID G. RETHWISCH[1]

Department of Chemical and Biochemical Engineering, University of Iowa,
Iowa City, Iowa 52242

Received June 21, 1991; revised October 28, 1991

Reaction kinetics under steady-state and transient conditions were used to study the effects of the catalyst (copper) and promoters (zinc and tin) on the direct reaction of methyl chloride with silicon to produce methylchlorosilanes. Use of infrared spectroscopy allowed rapid analysis of the gas-phase product composition. This allowed the accurate measurement of the apparent activation energy and the apparent reaction order for each product. An improved method for calculating direct reaction rates is also introduced. Addition of Zn as a promoter to Cu did not change the overall reaction rate but increased the selectivity for more methylated silanes. Tin promotion increased the selectivity for more chlorinated silanes, while having little affect on the overall reaction rate. Copromotion with zinc and tin increased the overall reaction rate; however, the selectivity for dimethyldichlorosilane (DMDC) was dependent on the concentration of tin. A trace amount of tin (ca. 0.005–0.01 wt%) produced the highest selectivity for DMDC; however, increasing the amount of tin to 0.2 wt% decreased the selectivity. We propose that the primary role of zinc is to direct the dissociative adsorption of MeCl such that the methyl group is attached to the Si and the Cl group is attached to the Zn.

INTRODUCTION

The majority of previous reaction kinetics investigations of the direct synthesis of organohalosilanes (the direct reaction)

$$2CH_3Cl + Si \rightarrow (CH_3)_xH_ySiCl_z \quad (\text{where } x + y + z = 4)$$

were aimed at providing the necessary data for industrial operation (*1–11*). In general, gas chromatography (GC) was used to determine the product composition. However, the separation of the silanes is demanding, resulting in analysis times of 15–60 min per data point. This significantly limits the time resolution of data acquisition. In the direct reaction, the catalyst and promoters are supported on silicon, which is a reactant. The support is constantly consumed and the surface is constantly changing; therefore, the reaction is never at "steady state" for any appreciable time. Indeed, at higher conversion (>ca. 40% conversion of silicon) a significant decrease in the reaction rate has been observed (*1*). There is only a short window of a few hours in which to collect steady-state kinetics, and even those data must be treated carefully as the overall activity may decrease with time. In many cases this has limited studies so that only one set of reaction conditions could be investigated for each sample. This is particularly problematic as it is difficult to obtain reproducible behavior from sample to sample. The long analysis times also limited the study of the behavior during the initial transient kinetics (often referred to as the induction period). The induction period typically lasts less than 1 h; therefore, GC analysis would allow no more than a few data points to be examined during this time.

Recently, Friedrich *et al.* (*12*) demonstrated that infrared spectroscopy (IR) can

---

[1] To whom correspondence should be addressed.

0021-9517/92 $3.00

be used to rapidly follow changes in the gas-phase composition of the product stream in the direct reaction. Specifically, IR provides compositional analysis comparable to results from GC; however, sample composition can be measured every 15 s rather than every 15–60 min. The improved sampling speed allows a broader range of reaction conditions to be studied on a single sample, leading to reduced error in studies of the apparent activation energy, the apparent reaction order, and the transient kinetics.

The reaction kinetics experiments that resulted were used to determine the effect of catalyst and promoters in the direct reaction and to study the apparent reaction order. Copper is commonly accepted as the catalyst of choice for the formation of dimethyldichlorosilane (DMDC, the desired product in the direct reaction). Recently, it was reported that a copper–silicon contact mass copromoted with zinc and tin was several times as active as an unpromoted CuSi mass, while also giving increased selectivity and stability (*13, 14*). The exact nature of this synergistic behavior is not fully understood. Therefore, this research is focused on the role of copper as a catalyst and on the roles of promoters in the contact mixture system.

EXPERIMENTAL

High-purity polycrystalline silicon (Union Carbide, 80–100 mesh, 0.5 m^2/g, 99.99% pure) was acid-treated prior to use to remove surface impurities and the native silicon oxide layer (*14*). Contact masses were prepared using a ball-milling method or by impregnation. The ball milling method was similar to that reported by Ward *et al.* (*14*). Briefly, $CuCl \cdot 2H_2O$ (Aesar, 99.99% pure) and promoters $SnCl_2 \cdot 2H_2O$ (Aesar, 99.9% pure) and $ZnCl_2 \cdot \frac{1}{2}H_2O$ (Aesar, 99.9% pure) were mixed with hexane and ball-milled for 24 h. This slurry was poured over the cleaned silicon, and the hexane was removed under vacuum at 373 K. For impregnation, the metal chloride to be added was dissolved in acetone, and the solution was poured over the pure silicon powder or the preprepared copper–silicon contact mass. The acetone was removed under vacuum at 373 K. In all cases, Cu was added by the ball-milling method. Several samples were also prepared with anhydrous salts. The results for hydrated or anhydrous salts were essentially the same.

Sample names were derived from their compositions. For example, CuZnSnSi(5/0.5/0.01) is a sample containing 5 wt% Cu, 0.5 wt% Zn, 0.01 wt% Sn, and the balance (94.5 wt%) Si. High-purity silicon and reagents were used to minimize the uncertainty due to the impurities, which may significantly affect the catalyst performance. An asterisk added to a sample name (e.g., ZnSi*(3/97)) indicates that the sample was prepared by the impregnation method.

Reaction kinetics were measured using the continuous, fixed-bed reactor system described in detail elsewhere (*12*). To ensure rapid heat transfer, a 0.25-in.-o.d., 0.18-in.-i.d. stainless-steel tube was used for the reactor. For these studies, ca. 2 g of freshly prepared contact mass was loaded in the reactor and pretreated (activated) in flowing helium at 603 K for 3 h. Following activation, the reactor was cooled to room temperature, evacuated, and the flow of methyl chloride (Matheson, 99.9% pure) was initiated. Helium (Air Products, 99.998% pure), was purified by passing through Ridox and 4A molecular sieves, and methyl chloride was used as received. The reactor was then heated at 10 K/min to the desired reaction temperature. To determine the onset reaction temperature (the temperature at which products were initially observed) and to determine relative rates of methyl and chlorine group deposition, transient reaction kinetics were measured during the initial heating. The steady-state condition was defined as the point when the activity and selectivity remained unchanged (<5%) for ca. 2 h. Ambient pressure and reaction temperatures from 523 to 623 K were used. To eliminate external diffusion limitations, flow rates greater than 3 cm^3/min were used.

The reactor effluent was analyzed by on-line GC or IR, although primarily IR was used. GC conditions are described in detail elsewhere (*12, 15*). The IR data were collected using a Mattson, Polaris infrared spectrometer. Spectra were collected at 4 cm^{-1} resolution. The IR gas cell was maintained at 373 K to prevent condensation of desorbed gases and to provide a uniform temperature for product analysis. Gas lines to the IR were heated to >373 K to prevent condensation of products. The spectra were quantified using a partial component regression method (Mattson, MQUANT). Infrared cannot detect chlorine (Cl_2) or hydrogen (H_2); however, previous studies using GC for detection indicate that these gases are not present under these conditions. For some samples, traces (<2 mol%) of disilanes were observed in both GC and IR; however, these peaks were weak and no standards were available for reliable quantitation. In addition, there may have been partial condensation in the gas cell and lines; however, materials in the IR cell prohibited higher operating temperatures.

Several contact masses were examined to see if the sequence of temperature change effected the observed results. The overall reaction rate was independent of the order of change of the reaction temperature. The selectivity for DMDC obtained during decrease of the reaction temperature were lower than those obtained when an increasing temperature is used. When the reaction was performed for long time periods (ca. 2 h) at a certain decreased reaction temperature, the selectivity for DMDC became similar to that for the case of increasing temperature. Therefore, only the data collected while increasing the temperature are reported.

CALCULATION OF RATE

A variety of methods have been used in the literature to calculate the conversion and the reaction rate for silane products. Most of these calculations assumed DMDC was the only product. These methods are strictly applicable only if the selectivity for DMDC is near 100%. In this case, due to the change in the number of moles of gas during reaction, the mole balance on methyl chloride gives

$$\text{Conversion } (X_{\mathrm{MeCl}}) = \frac{1 - y_{\mathrm{MeCl}}}{1 - (y_{\mathrm{MeCl}}/2)} \qquad (1)$$

$$\text{Reaction rate } (-r_{\mathrm{MeCl}}) = \frac{F_{\mathrm{in}}}{W_{\mathrm{cat}}} X_{\mathrm{MeCl}}, \qquad (2)$$

where y_{MeCl} is the mole fraction of MeCl in the product stream, r_{MeCl} is in gmol of MeCl consumed per s per g of contact mass loaded, F_{in} represents the reactant feed rate (in gmol/s), and W_{cat} is g of contact mass loaded. However, in many cases the selectivity for DMDC is 50% or less. In this case, calculations using the above equations may involve considerable error (up to 30%). In addition, the conversion is calculated using only the reactant concentration. Since MeCl conversion is maintained below 10%, the calculations are based on a relatively small change in a large number, and significant error can result. Finally, the IR sensitivity for methylchlorosilane products is 10 times greater than that for MeCl. Thus, silane concentrations can be measured more accurately. These problems are avoided using the calculation method described below.

For this study, conversions were calculated based on material balances for chlorine or methyl groups. All of the observed reaction products are included in these balances. No assumptions of reaction stoichiometry are required. For the mass balance on Cl,

$$\text{total Cl in} = F_{\mathrm{in}} y_{\mathrm{MeCl,in}} \qquad (3)$$

$$\text{total Cl out} = F_{\mathrm{out}} \Sigma\, n_{i\mathrm{Cl}} y_i \qquad (4)$$

$$\begin{aligned} \Sigma\, n_{i\mathrm{Cl}} y_i &= y_{\mathrm{MeCl}} + y_{\mathrm{HCl}} + y_{\mathrm{DMCS}} \\ &\quad + 2y_{\mathrm{DMDC}} + 2y_{\mathrm{MDCS}} + 3y_{\mathrm{MTCS}} \\ &\quad + 4y_{\mathrm{QCS}} + 3y_{\mathrm{TCS}} + y_{\mathrm{TMCS}}, \end{aligned} \qquad (5)$$

where $n_{i\mathrm{Cl}}$ is the number Cl atoms in species i, y_i is the mole fraction of species i in the product stream, and F_{in} and F_{out} are the total molar flow rates of reactants and products, respectively. The product species i are methane, HCl, dimethylchlorosilane

(DMCS), dimethyldichlorosilane (DMDC), methyldichlorosilane (MDCS), methyltrichlorosilane (MTCS), tetrachlorosilane (QCS), trichlorosilane (TCS), and trimethylchlorosilane (TMCS). This derivation neglects changes in the surface concentration of chlorine. As discussed above, disilanes and gas-phase cracking species such as H_2 and Cl_2 were assumed to be present in negligible amounts.

Assuming pure MeCl feed, the mole balance on Cl gives

$$\left(\frac{F_{\mathrm{out}}}{F_{\mathrm{in}}}\right)_{\mathrm{Cl}} = \frac{1}{\Sigma\, n_{i\mathrm{Cl}} y_i}. \qquad (6)$$

Hence, the MeCl conversion for a differential reactor can be obtained,

$$X_{\mathrm{MeCl,Cl}} = 1 - \left(\frac{F_{\mathrm{out}}}{F_{\mathrm{in}}}\right)_{\mathrm{Cl}} y_{\mathrm{MeCl}} = 1 - \frac{y_{\mathrm{MeCl}}}{\Sigma\, n_{i\mathrm{Cl}} y_i} \qquad (7)$$

and used with Eq. (2) to calculate the reaction rate. Similarly, the equation for the Me balance can be derived,

$$X_{\mathrm{MeCl,Me}} = 1 - \left(\frac{F_{\mathrm{out}}}{F_{\mathrm{in}}}\right)_{\mathrm{Me}} y_{\mathrm{MeCl}} = 1 - \frac{y_{\mathrm{MeCl}}}{\Sigma\, n_{i\mathrm{Me}}\, y_i}. \qquad (8)$$

For this calculation, a hydrogen atom in a species (e.g., HCl) was treated as one-third of a methyl group.

If $X_{\mathrm{Cl}} \neq X_{\mathrm{Me}}$ and, therefore, $r_{\mathrm{Cl}} \neq r_{\mathrm{Me}}$, the difference can be ascribed to the adsorption of Cl or Me on the catalyst surface. Hence, the increase of surface concentration of Cl or Me can be obtained, in particular, in the case of transient reaction conditions. The results calculated using the methyl and chlorine balances were essentially the same under steady-state conditions.

In general, the rate expression for the direct reaction has been assumed to be of the form

$$-r_i = \frac{k_i P^{n}_{\mathrm{MeCl}}}{(1 + \sqrt{K_A P_{\mathrm{MeCl}}} + K_{\mathrm{B}} P_{\mathrm{Silane}})^m}, \qquad (9)$$

where k_i is the apparent rate constant, K_i are adsorption equilibrium constants, P_i is partial pressure, and n and m are constants with n usually assumed to be 1 and $m = 2$. However, for low conversions $K_{\mathrm{B}} P_{\mathrm{Silane}} \ll 1$ and the equation can be approximated as

$$-r_i = k_i P^{q}_{\mathrm{MeCl}}, \qquad (10)$$

where q is the apparent reaction order. Equation (10) was used in this study to calculate the apparent reaction order.

RESULTS

Transient kinetics. Transient reaction kinetics for CuSi (10/90), CuZnSi (10/1), and CuZnSnSi (10/1/0.01) are shown in Fig. 1. A rapid increase in product formation was observed at temperatures of 525, 505, and 455 K for CuSi (10/90), CuZnSi (10/1), and CuZnSnSi (10/1/0.01), respectively (Fig. 1a). Therefore, promotion with zinc decreased the onset temperature, and copromotion with zinc and tin decreased the onset temperature even further. For all three samples, the direct reaction rate goes through an apparent maximum at ca. 570–600 K. This maximum results from the transient nature of the measurement. During these measurements the sample was heated at 10 K/min. Thus, the reported reaction rates include contributions from both reaction and temperature-programmed desorption. Figure 1b shows that for all samples, silanes are formed initially at ca. 420 K and go through a maximum selectivity at ca. 560 K with a shoulder at ca. 480 K. For the CuSi contact mass, the reaction rate calculated using the methyl balance was higher than that using the chlorine balance (Fig. 1a). However, for the others, the overall reaction rates calculated using both equations were the same. Previous studies in our lab indicate that a short induction period (5–15 min at 600 K for CuSi) is observed following the helium pretreatment; therefore, the transient kinetics were taken during the induction period. Comparison of results calculated using the methyl and chlorine balances suggests that the surface Cl concentration

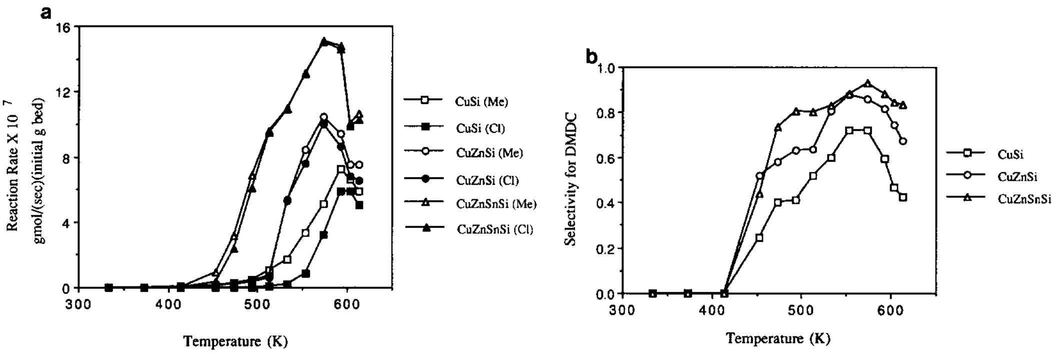

FIG. 1. Reaction rate and selectivity for DMDC as a function of temperature for the direct reaction over CuSi(10/90), CuZnSi(10/1), and CuZnSnSi(10/1/0.01): (a) reaction rate. Open symbols were calculated using methyl group balance, closed symbols were calculated using chlorine balance; (b) selectivity for DMDC calculated as the fraction of methylchlorosilane products. MeCl flow rates were 3 cm^3/min for CuSi(10/90) and 6 cm^3/min for CuZnSi(10/1) and CuZnSnSi(10/1/0.01). Lines are only intended to guide the eye.

for CuSi increased during the induction period, while it remained roughly constant for CuZnSnSi and CuZnSi.

Steady-state reaction kinetics. The results of steady-state reaction kinetics (Table 1) are similar to those reported previously (*1, 14, 15*). They have been included to show the reproducibility of the work and to indicate the selectivity and activity of the samples used in this study. Briefly, promotion with Zn increased the selectivity for DMDC while having little effect on the reaction rate. Zinc promotion via impregnation (which gave a sample with higher zinc dispersion than the ball-milling method) increased both activity and selectivity relative to CuSi. Copromotion with Zn and Sn (CuZnSnSi (5/0.5/0.01)) doubled the reaction rate and the selectivity for DMDC; however, increasing the tin loading further (CuZnSnSi (5/0.5/0.2)) decreased both the reaction rate and the selectivity. Addition of 0.3 wt% Sn to the 5 wt% Cu contact mass (CuSnSi*(5/0.3)), decreased the selectivity for DMDC by a factor of 3 relative to CuZnSnSi (5/0.5/0.01) with a corresponding increase in the formation of MTCS. The reaction rate was almost unchanged by addition of tin.

Zinc and tin were tested as catalysts in the absence of copper (Table 1). In the time scale of the experiment, pure silicon shows little reaction with methyl chloride and produces only CH_4 and HCl; no silanes were detected. Zinc as a catalyst (ZnSi*(3/97)) increased the decomposition rate of methyl chloride several times over that of pure silicon, but again no silane products were formed. The SnSi*(3/97) sample showed higher overall activity than ZnSi*(3/97) and it also produced various methylchlorosilanes. The primary product was CH_4 and the main silane products were MTCS and TCS. As the temperature was increased, selectivity for MTCS increased while that for TCS decreased. When zinc was added to the SnSi contact system (ZnSnSi*(3/1/96)), the activity was much higher than that for tin alone. The selectivity for MTCS was increased, but the selectivity for TCS was decreased, although the ZnSnSi* contact mass still produced primarily CH_4.

Reaction order. The apparent reaction order with respect to methyl chloride was determined for CuSi and CuZnSnSi and is reported in Table 2. The overall reaction (i.e., the consumption of MeCl) was ca. 1.6 order with respect to MeCl. The apparent reaction orders for the formation of CH_4, DMDC, and MTCS were similar to the overall reaction order. The apparent reaction order for

TABLE 1

Comparison of Reaction Rates and Selectivities for DMDC and MTCS in the Direct Reaction Obtained from Various Contact Masses at 573 and 613 K

Contact mass	573 K			613 K		
	Rate[a] ($\times 10^7$) mol/g · s	DMDC[b] (mol%)	MTCS[b] (mol%)	Rate[a] ($\times 10^7$) mol/g · s	DMDC[b] (mol%)	MTCS[b] (mol%)
CuSi(10/90)	1.2	54	29	4.2	38	36
CuSi(5/95)	0.5	58	28	2.2	41	37
CuSi(2/98)	0.3	55	31	1.1	40	37
CuZnSnSi(10/1/0.01)	4.7	89	9	9.6	83	11
CuZnSnSi(5/0.5/0.01)	2.1	88	9	5.8	78	13
CuZnSnSi(1/0.1/0.01)	0.7	65	14	1.4	60	17
CuZnSi(10/1)	1.4	70	13	4.3	54	20
CuZnSi*(5/0.5)	1.4	79	9	3.3	71	11
CuSnSi*(5/0.3)	0.6	19	72	3.0	14	70
CuZnSnSi*(5/0.5/0.2)	1.5	33	48	6.0	28	51
ZnSnSi*(3/1/96)	2.8	7	64	5.6	8	65
ZnSi*(3/97)	0.4	—	0.8	—	—	—
SnSi*(3/97)	0.7	13	28	1.6	11	47
pure Si	0.1	—	—	0.3	—	—

[a] Reaction rates in moles CH_3Cl consumed per second per gram of initial reaction mass; errors in reaction rates typically ca. 20%.

[b] Selectivity defined as ratio of moles of given product to total moles of analyzed silane product times 100; error in selectivity is typically <5 mol%.

production of TMCS was higher than the overall reaction order, while those for the hydrogen-containing silanes, DMCS and MDCS, were lower than the overall reaction order. The MeCl pressure had little effect on the selectivity for DMDC.

Activation energy. The apparent activation energies both for the overall reaction rate and for the formation of individual silanes using Arrhenius plots are summarized in Table 3. The activation energy values calculated for the CuSi samples were independent of copper loading. Adding tin to the CuSi system (CuSnSi*(5/0.3)) increased the activation energy, while copromotion with zinc and tin gave an activation energy lower than the CuSi or CuZnSi system. These results agree well with the data of Gasper-Galvin *et al.* (*15*), but are somewhat lower than values reported by others (*1, 3, 6, 14*). The activation energies were affected by the sample preparation method. Preparing samples by impregnation of zinc on the surface of the CuSi mass decreased the activation energy to a greater extent than preparation by ball-milling.

The apparent activation energies for each of the reaction products were also calculated. For CuSi the activation energy for DMDC formation was 20% lower than that for the overall reaction, and that for TMCS was 20% higher. The remaining products (CH_4, DMCS, MDCS, and MTCS) had activation energies that were comparable to the overall activation energy. Promotion with zinc (CuZnSi (10/1)) slightly decreased the activation energies for DMDC, MDCS, and TMCS but had no affect on the activation energies of the other silanes. When tin was added to the CuSi system (CuSnSi*(5/0.3)), all activation energies were increased by about 20% with the exception of MDCS, which doubled its activation energy. Also, for this sample, the activation energy of

TABLE 2

Apparent Reaction Orders for Overall and Individual Reactions for the Direct Reaction at 603 K over Cu (10/90) and CuZnSnSi (10/1/0.01)

Products	CuSi	CuZnSnSi
Overall	1.6 ± 0.2	1.7 ± 0.4
CH_4	1.6 ± 0.4	1.6 ± 0.6
DMCS	1.0 ± 0.3	0.5 ± 0.5
DMDC	1.7 ± 0.2	1.7 ± 0.3
MDCS	1.3 ± 0.5	0.6 ± 0.4
MTCS	1.5 ± 0.3	1.8 ± 0.4
TMCS	2.3 ± 0.4	2.3 ± 0.6

Note. The partial pressure range was 0.3 to 1.0 atm^{-1}. The data were fit using the power-law expression $r = kP^n_{MeCl}$.

DMDC was comparable to those for CH_4, MTCS, and TMCS. All activation energies obtained for the CuZnSnSi (10/1/0.01) system were reduced from those of CuSi (10/90) or CuZnSi (10/1).

Distribution of Cl, CH_3, and H groups in reaction products. The fraction of methyl groups, chlorine groups, and hydrogen groups included both in the total products (including methane) and in the silane products for each contact mass is calculated and shown in Table 4. The hydrogen fraction in the total products indicates the extent of decomposition of methyl chloride, since H atoms are produced by coking of surface methyl groups. Therefore, the ratio of H groups to CH_3 groups in the total products can be used as a measure of the extent of coking of methyl chloride on the surface. Higher temperature increased the H/CH_3 ratio for all contact masses, indicating more coking on the catalyst surface (as expected).

The apparent coking rate decreased as follows: ZnSi*(3/97) > SnSi*(3/97) > ZnSnSi*(3/1/96) > CuSnSi*(5/0.3) ≥ CuZnSnSi*(5/0.5/0.2) > CuSi (10/90) ≥ CuSi (5/95) > CuZnSi (10/1) ≥ CuZnSi*(5/0.5) ≥ CuZnSnSi (10/1/0.01). The overall coking rate of single metals during the direct reaction decreased in the order Zn > Sn > Cu. However, addition of zinc to the CuSi or SnSi system decreased the coking rates below those for the corresponding single metal contact masses. Therefore, Zn as a promoter decreased the coking rate while Zn in the absence of Cu increased the coking rate. This apparent anomaly is discussed in detail below.

As coking increased (as measured by H/CH_3 ratio) the Cl and H content in silane products increased for all contact masses, while the CH_3 group content decreased (Fig. 2). Zinc as a promoter increased the fraction of CH_3 in silanes but decreased Cl and H fraction, while tin as a promoter increased the fraction of Cl in silanes and decreased CH_3 and H fractions.

DISCUSSION

Results from the transient reaction kinetics indicated that the surface chlorine concentration of the CuSi contact mass increased during the initial stages of reaction. The promoted samples (CuZnSi and CuZnSnSi) did not show this effect, suggesting that promoters act in part by facilitating activation of the sample. Indeed, promotion with Zn or Zn and Sn has been shown to decrease the time required to activate the reaction mass (*14*). We also observed using TPR that Zn- or Sn-promoted samples (CuZnSi or CuSnSi) retained more chlorine during activation than CuSi samples (*16, 17*). Frank and Falconer (*11*) suggested that $SiCl_x$ surface species are the active sites for the direct reaction. The observed results (both TPR and transient kinetics) further suggest that surface chlorine is necessary for the direct reaction, that Zn and Sn promote the formation of these active sites, and that these sites are essentially formed during the activation treatment. In the absence of promoters, the CuSi samples sorbed additional chlorine during the induction period (transient kinetics) to form active sites containing Cl.

The apparent overall reaction order for the direct reaction was approximately 1.6 with respect to the MeCl pressure for both CuSi and CuZnSi. The apparent reaction

TABLE 3

Apparent Overall Activation Energy and Activation Energies for the Formation of Individual Products in the Direct Reaction Obtained for Various Contact Masses in the Temperature Range of 543 to 633 K

Contact mass	Overall	Activation energies[a] (kcal/gmol)							
		CH_4	DMCS	DMDC	MDCS	MTCS	TMCS	QCS	TCS
CuSi(10/90)	21	23	23	17	22	23	25	—	—
CuSi(5/95)	21	23	23	17	22	23	25	—	—
CuZnSi(10/1)	18	22	24	14	19	23	20	—	—
CuZnSnSi(10/1/0.01)	14	18	19	12	16	18	15	—	—
CuZnSnSi(5/0.5/0.01)	13	20	21	11	19	20	17	—	—
CuZnSi*(5/0.5)	15	21	21	13	18	20	23	—	—
CuSnSi*(5/0.3)	26	25	—	24	47	25	25	—	—
CuZnSnSi*(5/0.5/0.2)	25	27	—	15	45	25	21	—	—
ZnSi*(3/97)	18	—	—	—	—	—	—	—	—
SnSi*(3/97)	16	24	—	—	14	17	—	11	6
ZnSnSi*(3/1/96)	11	12	—	—	25	10	—	13	37
Pure Si	11	—	—	—	—	—	—	—	—
Pure Si[b]	14	11	—	—	27	24	—	21	11

[a] Error in activation energy is typically <20%; Values not given had too little product to give an accurate determination.

[b] Data from Frank and Falconer (*11*).

orders for DMDC, MTCS, and methane were ca. 1.5. However, the individual reaction orders for the hydrogen-containing silanes (DMCS and MDCS) were 1.0 and 1.3, respectively, and that for TMCS was 2.3. This is consistent with results in the literature (*1*), which show that a higher pressure of MeCl produced more methylated silanes. Operating at higher pressures also reduces the production of hydrogen-containing silanes. These results suggest that the mechanism for the chlorination, methylation, and hydrogenation steps in silane production are different. Specifically, TPR results suggest that Si–Me bonds in silanes result from direct adsorption of MeCl on the surface, while Si–Cl bonds require transfer of Cl to the silicon from other surface groups (*17*). This type of mechanism was first suggested by Andrianov *et al.* (*18*) and Klebansky and Fikhtengol'ts (*19*). This is discussed in more detail in the second paper in this series (*17*).

There has been considerable debate whether Zn promotes the direct reaction through a chemical or mechanical mechanism. The results in this study suggest that a chemical mechanism is responsible for at least some of the effects of zinc. In particular, promotion with zinc decreased the apparent activation energies for the overall reaction and for the formation of more methylated silanes (DMDC and TMCS) and increased the fraction of methyl groups in silane products. We propose that the primary role of zinc is to direct the dissociative adsorption of MeCl such that the methyl group is attached to the Si and the Cl group is attached to the Zn. TPR studies indicated that Zn was in the chloride form on the surface after the activation process (*16, 17*). Thus, Zn may act as a chlorine sink. In addition, electronegativity arguments indicate that MeCl should adsorb with the chlorine going to zinc and methyl group to Si or Cu (*20, 21*). When zinc is used as a catalyst, methyl groups chemisorb on the surface Si. However, in the absence of Cu, the Si–Si bonds are too strong to allow further reaction to form silanes. Therefore, the only available reactions for the sorbed methyl

TABLE 4

Distribution of Cl, CH_3, and H Groups in the Total Products and the Silane Products from the Direct Reaction at 573 K

Contact mass	Total products[a]				Silane products[b]		
	Cl (mol%)	CH_3 (mol%)	H (mol%)	H/CH_3	Cl (mol%)	CH_3 (mol%)	H (mol%)
CuSi(10/90)	46	42	12	0.29	55	40	4
CuSi(5/95)	46	43	11	0.26	55	41	4
CuZnSi(10/1)	48	45	7	0.16	51	45	4
CuZnSnSi(10/1/0.01)	49	48	3	0.07	51	48	1
CuZnSi*(5/0.5)	48	47	5	0.10	51	47	2
CuSnSi*(5/0.3)	44	39	17	0.43	67	33	tr[c]
CuZnSnSi(5/0.5/0.2)	47	39	16	0.41	62	35	3
ZnSi*(3/97)	33	17	50	3.03	—	—	—
SnSi*(3/97)	38	33	29	0.88	73	17	10
ZnSnSi*(3/1/96)	38	37	24	0.65	70	27	3

[a] Selectivity defined as ratio of moles of given product to total moles of all analyzed product times 100; error in selectivity is typically <5 mol%.

[b] Selectivity defined as ratio of moles of given product to total moles of analyzed silane product times 100; error in selectivity is typically <5 mol%.

[c] tr, Trace detected.

groups were cracking or hydrocarbon formation. Indeed, IR indicates only methane was observed in appreciable amounts for ZnSi*. When Zn is used as a promoter (i.e., CuZnSi) the methyl groups chemisorb on silicon sites. However, in this case the silicon is activated due to the presence of Cu–Si bonds. These "activated" Si–CH_3 species react further to form methylchlorosilanes rather than methane. Therefore, as observed, Zn alone on Si increases the cracking rate of methyl groups, while promotion with Zn decreases the cracking rate of methyl groups. The proposed ability of Zn to promote the adsorption of Me groups onto Si sites also accounts for the increased selectivity for DMDC observed for CuZnSi samples.

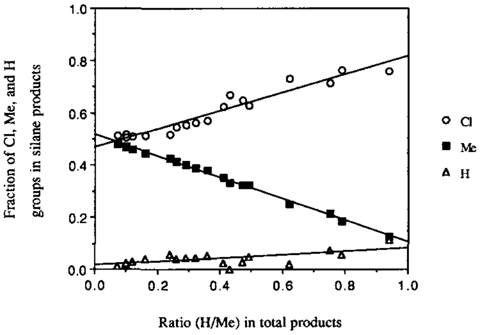

FIG. 2. Fraction of Cl, Me, and H groups in methylchlorosilane products versus H/Me ratio in the total products. Results for all samples and temperatures used in this study are included. Lines were fit using linear regression.

The ability to zinc to promote the adsorption of MeCl could result in an increase in the number of sorption sites or a change in the enthalpy of adsorption or the activation energy of adsorption for sorption sites. It is difficult to determine the number of active sites for these reaction samples. TPR results indicate that CuZnSi had 50% more total product desorbed than CuSi (17). However, it is unclear whether this was caused by an increase in the number of sites or by an increase in the fraction of sites occupied. In addition, all adsorption sites may not be active for the production of methylchlorosilanes. Without additional studies of the adsorption process, no direct conclusion as to the relative number of sites or the energetics of these sites can be made. Thus, this remains a fertile area for future study.

The SnSi* sample had a product distribution similar to that reported by Frank and Falconer (*11*) for the uncatalyzed reaction of pure silicon after extended exposure to MeCl (ca. 2-day activation period at 670 K). The presence of tin reduced the induction period from several days for pure silicon to <1 h for SnSi*. In both cases, highly chlorinated silanes (MTCS, TCS, and QCS) were the main products, and increasing the temperature increased the selectivity for MTCS while that for TCS decreased. Furthermore, the apparent overall activation energies were similar (see Table 3). This suggests that the reaction scheme for the formation of silanes for tin in the absence of copper is similar to that for pure silicon. Addition of Sn to pure Si lowered the activation energies for formation of the highly chlorinated silanes, which were the dominant methylchlorosilane products. Tin promotion of a CuSi contact mass (CuSnSi*) increased the production of chlorinated silanes relative to CuSi and decreased the induction period. This suggests that tin promotes the formation of Si–Cl species in methylchlorosilanes. The increased chlorine content in the methylchlorosilanes may be explained in part by the increased cracking of methyl groups over CuSnSi*; however, this does not explain the ability of tin to decrease the induction period. As mentioned above, Frank proposed that the active species for the direct reaction were $SiCl_x$ sites (*11*). We propose that the role of tin both alone and in the presence of Cu is to increase the surface transfer of Cl, thereby promoting the formation of the active $SiCl_x$ species and increasing the production of more chlorinated silanes. However, the ability of tin to increase surface transfer of Cl may be related to the ability of tin to change coordination number to accommodate additional ligands (*22, 23*).

Tin promotion (CuSnSi* vs. CuSi) increased cracking of surface methyl groups (as evidenced by the increased H/CH_3 ratio) but *decreased* the H fraction in silane products (Table 4). This apparent anomaly suggests that the concentration of methyl groups on tin containing areas was relatively high. As a result, surface H groups (resulting from cracking) are scavenged by these methyl groups to form CH_4 rather than reacting to form hydrogen-containing methylchlorosilane species.

Copromotion with zinc and tin increased the overall reaction rate by a factor 3 relative to CuSi. In addition, the apparent activation energies for DMDC and TMCS in CuZnSnSi samples were reduced by about 35% relative to CuSi while the apparent activation energies for the other products were essentially unchanged. The selectivity for DMDC from the CuZnSnSi contact system containing a trace amount of tin (0.005–0.01 wt%) was the highest of all the reaction masses. This result is consistent with the zinc–tin synergism for the copper-catalyzed reaction for Sn concentrations of 0.01–0.03 wt% (*13, 14*). However, when the amount of tin in the CuZnSnSi mass was increased to 0.2 wt% (CuZnSnSi*), the reaction rate remained high, but the selectivity for DMDC decreased. While this appears to be inconsistent with the literature, the Sn concentration in our sample was 10 times greater (*13, 14*). Indeed, increasing the Sn content in the CuZnSnSi* sample to 0.2 wt% shifted the apparent activation energy and product distribution to values more typical of CuSnSi*. The results in the CuZnSnSi system may be explained by the proposed roles and relative concentrations of zinc and tin. That is, (1) zinc increases the adsorption of methyl chloride and accelerates the formation of $Si–CH_3$ bonds in methylchlorosilane products and (2) tin increases the surface transfer of Cl and accelerates the reformation of the active $SiCl_x$ sites. Therefore, at low tin concentration DMDC was the dominant product, while at higher tin concentrations excess Si–Cl are formed, and the selectivity for DMDC is decreased while that for MTCS is increased.

CONCLUSIONS

Addition of Zn as a promoter to Cu (CuZn Si) did not change the overall reaction rate but increased the selectivity for more methylated silanes. Tin promotion increased the selectivity for more chlorinated silanes, while having little affect on the overall reaction rate. Copromotion with zinc and tin increased the overall reaction rate; however, the selectivity for dimethyldichlorosilane was dependent on the concentration of tin. A trace amount of tin (ca. 0.005–0.01 wt%) produced the highest selectivity for DMDC; however, increasing the amount of tin to 0.2 wt% decreased the selectivity. The results of this study suggest that the mechanism for the chlorination and methylation steps in silane production are significantly different. Specifically, methylation is proposed to occur directly by dissociative adsorption of MeCl with the methyl group attaching to Si. Formation of Si–Cl bonds is proposed to occur by surface transfer from adjacent chlorine-containing sites. We propose that the primary role of zinc is to direct the dissociative adsorption of MeCl such that the methyl group is attached to the Si and the Cl group is attached to the Zn.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Idaho National Engineering Laboratory, High Energy Chemistry Research Subcontract C87-101334. We are grateful to Union Carbide for providing the high-purity silicon. We also acknowledge the help of Professor H. Bruce Friedrich of the University of Iowa Department of Chemistry in developing the FTIR method and discussions with Timothy J. Wessel during the preparation of this manuscript.

REFERENCES

1. Voorhoeve, R. J. H., "Organohalosilanes, Precursors to Silicones." Elsevier, New York, 1967.
2. Ward, W. J., and Carroll, K. M., *Electrochem. Soc. J.* **129**(1), 227 (1982).
3. Frank, T. C. Kester, K. B., and Falconer, J. L., *J. Catal.* **91,** 44 (1985).
4. Singhania, P. P., Wattal, G. K., and Kunzru, D., *Chem. Eng. Sci.* **38**(3), 469 (1983).
5. Gorbunov, A. I., Belyi, A. P., and Filippov, G. G., *Russ. Chem. Rev.* **43**(4), 291 (1974).
6. Belyi, A. P., Gorbunov, A. I. Fel'dshtein, N. S., and Golubsov, S. A., *Russ. J. Phys. Chem.* **46**(2), 303, (1972).
7. Banholzer, W. F., Lewis, N., and Ward, W., *J. Catal.* **101,** 405 (1986).
8. Banholzer, W. F., and Burrell, M. C., *J. Catal.* **114,** 259 (1988).
9. Voorhoeve, R. J. H., Geertsema, B. J. H., and Vlugter, J. C., *J. Catal.* **4,** 43 (1965).
10. Voorhoeve, R. J. H., and Vlugter, J. C., *J. Catal.* **4,** 123 (1965).
11. Frank, T. C., and Falconer, J. L., *Langmuir* **1,** 104 (1985).
12. Friedrich, H. B., Sevenich, D. M., Gasper-Galvin, L. D., and Rethwisch, D. G., *Anal. Chim. Acta* **222,** 221 (1989).
13. Ward, W. J., Ritzer, A., Carroll, K. M., and Flock, J. W., U.S. Patent 4,500,724 (1985).
14. Ward, W. J. Ritzer, A., Carroll, K. M., and Flock, J. W., *J. Catal.* **100,** 240 (1986).
15. Gasper-Galvin, L. D., Sevenich, D. M., Friedrich, H. B., and Rethwisch, D. G., *J. Catal.* **128,** 468 (1991).
16. Kim, Jong Pal, Ph.D. dissertation, University of Iowa, 1990.
17. Kim, J. P., and Rethwisch, D. G., in preparation.
18. Andrianov, K. A., Zhdanov, A. A., Golubtsov, S. A., and Sololevskii, M. V., *Uspekhi Khim.* **18,** 145 (1949).
19. Klebansky, A. L., and Fikhtengol'ts, V. S., *Zh. Obshch. Khim.* **26,** 2502 (1956).
20. Pauling, L., "The Nature of the Bond." Cornell Univ. Press, New York, 1960.
21. Sanderson, R. T., "Chemical Periodicity." Reinhold, New York, 1960.
22. Poller, P. C., "The Chemistry of Organotin Compounds." Academic Press, New York, 1970.
23. Davies, A. G., and Smith, P. J., *in* "Comprehensive Organometallic Chemistry (G. Wilkinson, F. G. A. Stone, and E. W. Abel, Eds.), Vol. 2 Pergamon Press, Oxford, 1982.