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THE REACTION OF A METAL CHLORIDE WITH SILICON AND ITS CATALYTIC AND PROMOTIVE ACTIVITY IN THE DIRECT SYNTHESIS OF SILANES

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Summary

The reaction of some metal chlorides with silicon has been investigated in the temperature region of 200 - 500°C. It has been found that if the free enthalpy * of reaction is less than zero a quantitative relationship exist between the threshold temperature of the reaction of the metal chloride with silicon and the product of the average standard free enthalpy of formation per gram atom chlorine bound to the metal times the temperature in K at which the vapour pressure of the metal chloride is 1 mm Hg. It has further been found that there exists a relationship between the reaction threshold temperature and the catalytic activity of some metals in the direct synthesis of silanes. The effect of some metal chlorides as a promoter can also be explained on thermodynamic grounds.

Introduction

The direct synthesis of organochlorosilanes, which are the precursors to silicones, involves the use of catalysts which are present on the silicon surface as a metal (Cu, Ag) or as an intermetallic compound (CU: η-phase [1]). The action of the catalyst involves an interaction of the metal with the gas phase followed by chemisorption of the alkyl (or aryl) chloride and subsequent chlorination or alkylation (or arylation) of the silicon or other reaction intermediates present on the surface [1]. Recently it has been suggested that the reaction should be regarded as a chain reaction on the contact mixture surface starting at an active site, e.g., $\dot{\text{Si}}\text{Cl}$, the active sites being continuously regenerated during the synthesis [2, 3]. If the interaction of the metal with the gas phase results in a dissociative chemisorption of the alkyl (aryl) chloride, or if cracking of the organic ligand takes place, then the metal chloride can be formed on the contact mixture surface. An example of the latter behaviour is

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* The term "free enthalpy" used in this paper is equal to the term "Gibbs energy".

provided in eqn. 1, the direct synthesis of methylchlorosilanes with copper as catalyst:

$$2\,Cu(CH_3Cl) \rightarrow 2\,CuCl + CH_4 + H_2 + C \tag{1}$$

Furthermore, the metal chloride may be present on the surface as a reaction intermediate in the chain reaction. During the synthesis, the reaction must not be interrupted at any stage, and this means that there must be the possibility of reaction between the metal chloride and the (substituted) silicon, preferably in every reaction step. In such a case the overall free enthalpy of reaction (ΔG_r) of reaction 2 should preferably be negative, or, at least only slightly positive. (MCl_n = metal chloride with n chlorine atoms bound to the metal).

$$m\,MCl_n + \frac{m \cdot n}{4}\,Si \rightarrow m\,M + \frac{m \cdot n}{4}\,SiCl_4 \tag{2}$$

One has to keep in mind, however, that this is only a necessary condition for the occurrence of the reaction and not a guarantee that reaction will take place. Other factors, such as particle size, can also influence the reaction kinetics; also, for one or several reaction steps, the change of free enthalpy may be far greater than zero, thus inhibiting the further course of the reaction. Summarising, every reaction step of the following type (eqns. 3 and 4) must be kinetically possible in order to guarantee a reasonable reaction rate for the direct synthesis:

$$MCl_n + Si \rightarrow MCl_{n-1} + SiCl \tag{3}$$

$$SiCl + \begin{matrix} MCl_n \\ MCl_{n-1} \end{matrix} \rightarrow SiCl_2 + \begin{matrix} MCl_{n-1} \\ MCl_{n-2} \end{matrix} \tag{4}$$

etc. That reaction intermediates of the type $SiCl_n$ exist on the contact mixture surface has been demonstrated elsewhere [4, 5].

Little is known about these reactions. The reaction between a metal chloride and silicon is, under the conditions of the investigation, a solid/solid or a liquid/solid reaction which may be accelerated by the transport of the metal chloride to the silicon via the gas phase. For these reactions there is a threshold temperature above which the reaction proceeds very rapidly, sometimes even violently. It should be emphasized that this threshold temperature is not the temperature of the beginning of the reaction but the temperature at which a marked rate of reaction can be observed [6, 7]. The threshold temperature may depend on the history of the system, impurities in the reacting substances, impurities in the gas phase, etc. [6]. Furthermore, there is the complication that the oxide layer, always present on the silicon, may hamper the start of the reaction [8].

Of the reactions under investigation, most is known about that between CuCl and silicon, because it can be used to prepare a reactive contact mixture for the synthesis of silanes [1]. The reaction threshold temperature varies from 180 to 400° [7, 9 - 11]; the normal temperature, using fresh copper chloride and performing the reaction under a nitrogen atmosphere, is 300° [11]. Furthermore, the temperatures of the onset of the reactions of $PbCl_2$ and $SnCl_2$ with silicon have been found to be about 360 and 350°, respectively [12]. Copper, lead and tin are known to be catalytically active in the direct synthesis of methylchlorosilanes, each catalyst yielding a different main product [12]. Therefore it seemed to be of interest to investigate the reaction of some metal chlorides with silicon in order to find a theoretical basis for the choice of catalyst for the direct synthesis of silanes.

Experimental

Apparatus

The equipment shown in Fig. 1 was used. Two thermocouples, one in the spherical shaped glass reactor A, the other in the reference reactor B, are connected in opposing polarity. The temperature of the system is measured by another thermocouple situated in reactor B. By measuring the heating curve of the system, the threshold temperature of an exothermic reaction can be detected very accurately because the spherical shape of the reactor prevents the heat of the reaction from dissipating easily, and a peak will occur in the thermogram on the recorder. The threshold temperature of an endothermic reaction is more difficult to determine in this way because the negative heat effect causes the reaction to slow down. When the heat production of a reaction was negative, the reaction threshold temperature was determined as the temperature at which the first reaction products appeared in the CO_2/acetone-cooled product vessel. Heating of the reactors was by a fluidised bed of silicon. The reaction products were removed from the reactor with dry oxygen-free nitrogen.

Materials

The silicon used in the experiments was technical grade, the main impurities

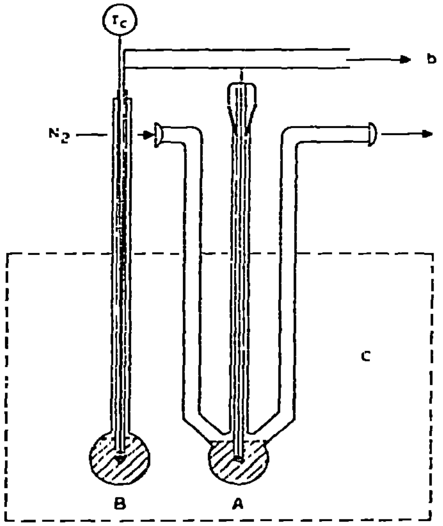

Fig. 1. Apparatus for measuring the temperature of the start of the reaction between a metal chloride and silicon. A = reactor; B = reference reactor; C = fluidised bed of silicon; N_2 = stream of purified nitrogen; a = product stream to product vessel; b = millivolt signal to recorder; Tc = thermocouple for temperature measurement.

being 0.4% Fe, 0.1% Al and 0.3% Ca + Mg (by weight), and before use it was washed with distilled water, dried, and treated with a magnet to remove part of the iron (resulting in an iron content of 0.2-0.3 %). Unless indicated otherwise, the particle size of the silicon consisted of the sieve fraction 50-75 microns. The reference reactor was filled with pure silicon (10-15 g), the reactor itself was filled with 10-15 g of the silicon/metal chloride mixture. The metal chlorides used were fine powders (particle diameter < 50 microns) and were chemically pure (Merck). If necessary they were dried. CuCl was prepared from $CuSO_4$, Cu and HCl; AgCl from $AgNO_3$ and HCl. Before heating, the mixture was dried at 50-100° during 16 h under a stream of purified nitrogen.

Results and discussion

To indicate the accuracy of the experiments some measurements of melting points of metal chlorides and mixtures thereof are given in Table 1; there is good agreement with published values. Only in the case of $ZnCl_2$ does disagreement exist. However, melting points of $ZnCl_2$ can be found in the literature ranging from 262 to 330° [15]. Some measurements of melting points are shown in Fig. 2.

The most relevant data are summarised in Table 2. Some heating curves are shown in Fig. 3. $RbCl_2$ and $ZnCl_2$ were also investigated, but because the free enthalpy of reaction in the temperature region up to 500° is greater than zero no reaction took place, as expected.

Under the applied conditions the chlorides of copper, CuCl and $CuCl_2$, start reacting with silicon at about 300°. Mixing with $SnCl_2$ reduces this temperature for CuCl to 250°, the lowest threshold temperature being 180° [9]. The product mixture resulting from the reaction of the copper chlorides with silicon does not consist solely of $SiCl_4$, appreciable quantities (10-20%) of Si_2Cl_6 and Si_3Cl_8 are also formed. The latter products were formed in all the reactions except that between $CdCl_2$ and silicon, in which $SiCl_4$ was formed almost exclusively. Above 200° copper is used as a catalyst in the production of chlorosilanes, above 260° in the production of methylchlorosilanes, and above 400° in the production of phenylchlorosilanes [1].

AgCl starts reacting with silicon at 430°; mixing AgCl with $SnCl_2$ reduces the reaction threshold temperature of the AgCl reaction with silicon to 315°. At a temperature above 400° silver is known to be a catalyst in the direct

TABLE 1

MEASUREMENTS OF MELTING POINTS OF METAL CHLORIDES AND MIXTURES THEREOF

MCl_n	MCl_n (gm)	Si (gm)	dT/dt (°C/min)	M.p. (°C)	Lit. M.p. (°C)
AgCl	2.5	10.0	2.5	455	454 [a]
$SnCl_2$	3.0	10.0	0.9	246	246 [a]
$ZnCl_2$	4.2	10.0	2.0	294	283 [a]
CuCl $SnCl_2$	1.7 1.7	10.4	2.1	170	172 [b]

[a] Ref. 13. [b] Ref. 14.

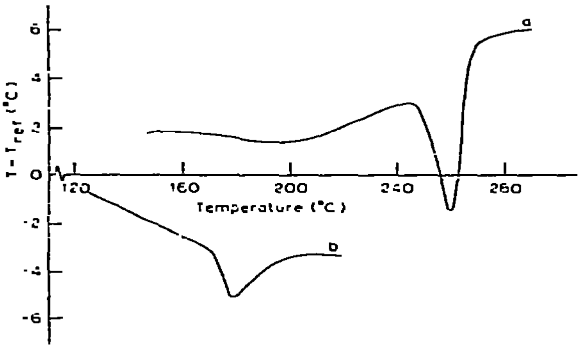

Fig. 2. Heating curves of $SnCl_2$ and a mixture of $SnCl_2$ and CuCl. a = $SnCl_2$; b = $SnCl_2$ + CuCl.

synthesis of phenylchlorosilanes [1, 16]. At lower temperatures pure silver cannot be used as a catalyst because of the slow chlorine transfer to silicon.

$PdCl_2$ and $CoCl_2$, with reaction threshold temperatures of 350 and 430°, respectively, are not known to be catalysts for the direct synthesis, but are, in view of their threshold temperatures, possible catalysts for the production of phenylchlorosilanes.

$HgCl_2$, which starts reacting at 226°, is not known to be a catalyst and is probably too volatile to be used. $SnCl_2$ (reaction threshold temperature 300°)

TABLE 2

SUMMARY OF EXPERIMENTAL DATA AND RESULTS

Exp. no.	Si (gm)	MCl_n (gm)	dT/dt (°C/min)	T_{start} (°C)	Reaction enthalpy
1	90.0 [a]	15.4 CuCl	2.0	300	negative
2	13.0	2.0 $CuCl_2$	2.5	310	negative
3	10.6	2.2 $CuCl_2 \cdot 2aq$ [b]	1.5	295	negative
4	10.2	3.0 $FeCl_3$	2.0	240 [c] 450 [c]	negative positive
5	10.0	3.0 $CdCl_2$	1.8	480	positive
6	10.2	3.0 $PbCl_2$	1.2	390	positive
7	10.0	2.0 $PdCl_2$	1.3	350	negative
8	10.0	2.5 AgCl	2.5	456	negative
9 [d]	10.0	2.6 AgCl	2.2	430	negative
10	10.5	2.5 $CoCl_2$	1.2	432	negative
11	10.0	3.0 $SnCl_2$	0.9	300	positive
12	10.7	2.7 $HgCl_2$	2.0	226	negative
13	10.4	1.7 CuCl 1.7 $SnCl_2$	2.1	250	neg/pos
14 [e]	7.0	3.0 AgCl 3.1 $SnCl_2$	2.7	315	neg/pos

[a] The temperature of the start of the reaction was measured in the equipment described in ref. 1. Particle size of the silicon 50-250 microns. [b] $CuCl_2 \cdot 2aq$ was dried in the reactor after mixing with silicon. [c] Reaction of $FeCl_3$ with silicon takes place in two steps: the first reaction step stops with the formation of $FeCl_2$ (exotherm); further heating results in the formation of iron (endotherm). [d] Particle size of silicon 75-105 microns; not dried during 16 h. [e] Particle size of silicon 75-105 microns.

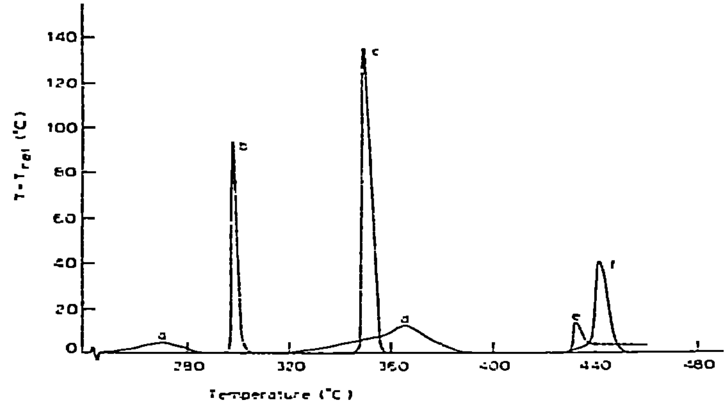

Fig. 3. Heating curves of some metal chloride/silicon mixtures. a = $CuCl/SnCl_2$; b = CuCl; c = $PdCl_2$; d = $AgCl/SnCl_2$; e = $CoCl_2$; f = AgCl.

is known to be a catalyst for the production of methylchlorosilanes above 300° [12]. $PbCl_2$ (reaction threshold temperature: 390°) has been used as a catalyst for the production of methyl- and phenyl-chlorosilanes at temperatures above 400° [12, 23]. At lower temperatures $PbCl_2$ is an inhibitor for the reaction [17].

For the production of chlorosilanes, iron is an interesting possible catalyst because it is always present in the silicon as a contaminant. For the reaction of $FeCl_3$ with silicon, a free enthalpy of reaction of −81 kcal/mol $SiCl_4$ can be calculated (T = 500 K). Thus, viewed thermodynamically, $FeCl_3$ can react completely with silicon to form $SiCl_4$. The standard free enthalpies of formation of $FeCl_3$(c) and $FeCl_2$(c) are, however, −69.9 and −66.1 kcal/mol, respectively [18]. Apparently the greatest decrease in free enthalpy in the reaction of $FeCl_3$ with silicon will result from the conversion of $FeCl_3$ into $FeCl_2$. If there is a steady trend, from the $FeCl_3$ to $FeCl_2$ conversion to the $FeCl_2$ to FeCl conversion, then it is to be expected that reaction step 5 will be rate limiting, because in this step

$$FeCl + SiCl_n \rightarrow Fe + SiCl_{n+1} \qquad (5)$$

the decrease in free enthalpy will be low, and at lower temperatures the change in free enthalpy of this step may even be positive. Indeed, at 240° $FeCl_3$ starts reacting exothermically with silicon, but the reaction stops with the formation of $FeCl_2$; heating for some hours at 350° does not cause further reaction. The endothermic reaction of $FeCl_2$ with silicon occurs only at a temperature of 450°. Because of this, iron cannot be used as a catalyst at temperatures below about 450°, and even at a temperature of 500° it proves to be a poor catalyst [19].

Another interesting metal is cadmium, because between 700 and 800 K the sign of the free enthalpy change of the reaction of $CdCl_2$ with silicon changes from positive to negative. $CdCl_2$ starts reacting with silicon at a temperature of 480°. At lower temperatures $CdCl_2$ is known to be a very good promoter in the direct synthesis of organochlorosilanes [20-22]; at about 450° its action as a promoter changes, and cadmium becomes a catalyst for the production of methyl- and phenyl-chlorosilanes [24].

As can be seen from the experimental results a clear qualitative relationship exists between the threshold temperature of the reaction of a metal chloride with silicon and the catalytic activity of the metal in the direct synthesis of chlorosilanes; that is, the lower the reaction threshold temperature, the lower the temperature at which the metal may become catalytic.

Promoters in the direct synthesis

It has been shown above that for a catalyst to be active in the direct synthesis of chlorosilanes transfer of chlorine from the metal to silicon must be possible in every reaction step. If this is not the case it may still be possible to transfer some chlorine to the silicon in the initial reaction steps, because it is to be expected that in these steps the greatest decrease in free enthalpy can be obtained. Using $CdCl_2$ as a promoter, for example:

$$CdCl_2 + Si \rightleftharpoons CdCl + SiCl \quad (6)$$

$$CdCl_2 + SiCl \rightleftharpoons CdCl + SiCl_2 \quad (7)$$

$$CdCl + Si \rightleftharpoons Cd + SiCl \quad (8)$$

In this way active sites can be created, being the starting centres of the chain reaction on the contact mixture surface. Also the promoting action of $ZnCl_2$, $AlCl_3$ and $SbCl_3$ in the direct synthesis can be explained by reactions of the type given above.

Quantitative correlation of the experiments

A quantitative relationship has been established which relates the reaction threshold temperature of a metal chloride with silicon to some physical properties of the reacting substances. The most important properties besides, for example, particle size, are the vapour pressure and melting point of the metal chloride. A high vapour pressure and a low melting point result in a good distribution of the metal chloride on the silicon surface. Another important quantity is the change in free enthalpy of the system. If $\Delta G_r > 0$ there will be little tendency for the reaction to proceed under the conditions of the direct synthesis.

A relationship has been found between the threshold temperature of the reaction of a pure metal chloride with silicon and the product of the average standard free enthalpy of formation per gram atom chloride bound to the metal (ΔG_f°/Cl) times the temperature in K at which the vapour pressure of the metal chloride amounts to 1 mm Hg (see Fig. 4). If $\Delta G_r < 0$ the reaction threshold temperatures can be found using eqn. 8 (standard deviation 32.3°C)'.

$$T_s\,(^\circ\mathrm{C}) = 194.3 - 0.0072 \times \{\Delta G_f^\circ/\mathrm{Cl}\} \times T_{1\,\mathrm{mm}}\,(\mathrm{K}) \quad (9)$$

The constants in this equation were calculated by the method of least squares. Vapour pressures and ΔG_f° have been taken from ref. 13. ΔG_f° of $PdCl_2$ and $SnCl_2$ have been estimated from ΔH_f°. ΔG_f° values of $CuCl_2$, $FeCl_2$ and $FeCl_3$ have been taken from ref. 18. For the reaction of $FeCl_3$ with silicon the ΔG_f° for transfer of the last chlorine atom has been used.

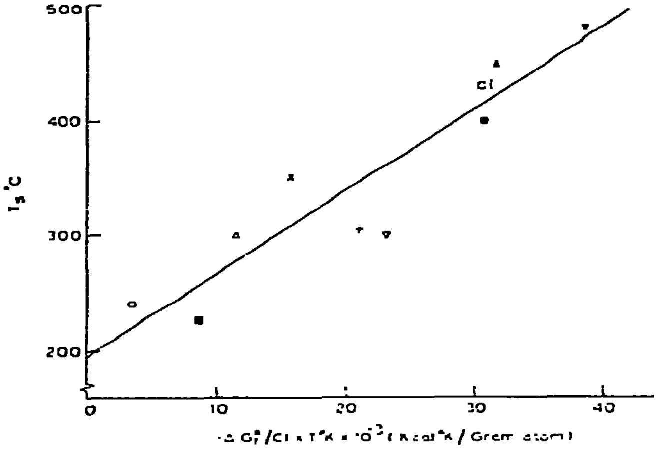

Fig. 4. Quantitative correlation of the temperatures of the start of the reaction of metal chlorides with silicon. ○ = $FeCl_3$; ■ = $HgCl_2$; Δ = $CuCl_2$; + = $SnCl_2$; ∇ = $CuCl$; X = $PdCl_2$; ● = $PbCl_2$; □ = $CoCl_2$; I = $AgCl$; ▲ = $FeCl_2$; ▼ = $CdCl_2$.

Conclusions

It has been demonstrated that a relationship exists between the threshold temperature of the reaction of a metal chloride with silicon and the catalytic activity of the metal in the direct synthesis of chlorosilanes. A quantitative prediction of the reaction threshold temperatures is possible if some basic properties of the metal chlorides are known. A possible catalyst can thus be selected on a thermodynamic basis, and the effect of a promoter can be explained on a similar basis. A pure metal may exhibit catalytic properties only if the chlorine transfer to silicon is possible in every reaction step. If this is not the case the metal chloride may still be able to act as a promoter.

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