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NOTE

KINETICS AND SYNTHESIS MECHANISM OF DIMETHYLDICHLOROGERMANE

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INTRODUCTION

Organochlorogermanes, important for preparation of organogermanium compounds, can be prepared by the direct interaction of germanium with the corresponding halogen derivatives[1]. Much work[2-13] has been devoted to investigation of the synthesis by the method of the methylchlorogermanes.

Pure germanium does not react[1] with methyl chloride up to 460°; at 505–520°, methyl chloride decomposition and methyltrichlorogermane formation[9] take place. The best catalyst is copper, (as in the case of methylchlorosilane synthesis) it is used in amounts up to 45% of the contact mass[1,11]. In the presence of copper the reaction proceeds rapidly at 320–360° and the main reaction product is dimethyldichlorogermane (70–75%); its yield decreases with increasing copper content and rise in temperature[11]. Additives such as $ZnCl_2$, Sb and As in the contact masses promote methyltrichlorogermane formation (up to 70%)[2], whereas in the methylchlorosilanes synthesis they increase the yield of dimethyldichlorosilane[14-16]. By control of the composition of the contact mass content and the reaction temperature the synthesis may be directed to preferential formation of either methyltrichlorogermane (up to 70%) or dimethyldichlorogermane (up to 70%)[10-12].

In the studies mentioned above contact masses containing the mixture of germanium and copper were used. The use of alloys was not investigated although silicon–copper alloys are commonly used in the synthesis of methylchlorosilanes.

There are no data on the reaction kinetics in the literature. The problem of the present work was to investigate the kinetics of the dimethyldichlorogermane synthesis using contact masses prepared in different ways, and to establish the characteristics of the reaction for comparison with those of the analogous reaction for silicon.

EXPERIMENTAL

Pure (99.999%) polycrystalline germanium and powdered copper (trade mark PM-2 ~99.6%) were used. Alloys were prepared from high pure copper grade V3

TABLE 1

THE DEPENDENCE OF THE CONDENSATE COMPOSITION ON THE REACTION TEMPERATURE AND PROPORTION OF COPPER

$P(CH_3Cl) = 650–700$ mm

Temp. (°C)	Mixture of powders (Cu 27%)			Alloy (Cu 30%)			Alloy (Cu 13.5%)		
	$(CH_3)_3GeCl$	CH_3GeCl_3	$(CH_3)_2GeCl_2$	$(CH_3)_3GeCl$	CH_3GeCl_3	$(CH_3)_2GeCl_2$	$(CH_3)_3GeCl$	CH_3GeCl_3	$(CH_3)_2GeCl_2$
320				0.3	1.0	98.7			
340				0.7	1.7	97.6			
360			100	1.5	2.2	96.3	2.3	8.2	89.5
380	2.6	3.0	94.4	1.0	1.5	97.5	2.0	6.7	91.3
400	4.6	5.4	90.0	0.7	1.0	98.3	1.3	5.2	93.5
420	2.9	25.6	71.5					1.9	98.1

(impurity content $< 10^{-2}\%$) and germanium in a graphite crucible, and were subsequently pulverized (50–250 μ) in an agate mortar. The copper content was determined by polarography[17]. Mixtures of germanium (50–250 μ) and copper (1–5 μ) powders were prepared by hand.

Commercial methyl chloride was purified and dried in traps with sulphuric acid and KOH. The CH_3Cl content of the purified product was shown by chromatographic analysis to be 99.8%[18].

The quasi-static circulation apparatus earlier used by us for studying synthesis kinetics of trichlorosilane[19,20] was used. The contact masses (16–30 g) placed in the reactor and dried at 180° for 4 h in vacuum (10^{-2} mm). The temperature was raised to the desired level and methyl chloride was fed into the system, the rate of the reaction being controlled by the pressure drop in the system. The products were frozen out in a trap cooled with dry ice and acetone and were analyzed by chromatography[21].

RESULTS AND DISCUSSION

Before kinetic experiments were begun, conditions for the selective formation of dimethyldichlorogermane were established. As can be seen from Table 1, it formed 90–98% of the product at temperatures of 320–400°, and the proportion did not depend upon the state of the copper in the contact masses or on its concentration (in the range of 3–30%). The studies of the kinetics were carried out in this temperature range, and the data below thus refer to the reaction forming dimethyldichlorogermane.

The influence of the pressure of methyl chloride on the reaction rate (Table 2) has been examined in the range of 250–700 mm at 340–380°, at which the process proceeds at a measurable rate and carbonization of the contact mass is low.

TABLE 2

DEPENDENCE OF THE RATE OF FORMATION OF DIMETHYLDICHLOROGERMANE ON THE METHYL CHLORIDE PRESSURE

Contact mass type	Cu (%)	Temp. (°C)	Pressure of CH_3Cl (mm)	Rate, W (10^3 mmol·g^{-1}·min^{-1})	Reaction order for CH_3Cl, n
Mixture of powders	27	340	250–700–250	0.4–1.7–0.4	1.4
GeCu alloy	3.0	380	250–700–250	0.4–2.8–0.5	1.8
	13.5	370	250–700–250	0.65–2.9–0.65	1.4
	30.0	355	300–690–300	0.5–2.0–0.6	1.6
	30.0	360	250–700–250	0.4–2.3–0.4	1.7

Since, as with silicon[22], the reaction rate is likely to change as the contact mass reacts and its specific surface increases, the experiments were carried out with low conversion of germanium and methyl chloride (see Table 2, columns 4, 5), as in studies of the trichlorosilane synthesis[19,20]. The methods used for the trichlorosilane synthesis were used in studying the temperature dependence of the reaction rate (see Table 3, columns 4, 5).

As is seen from the data of Tables 2 and 3 the order of reaction with respect to methyl chloride is about 1.5, and the activation energy (E) is 24.0–27.5 kcal/mol. Both

TABLE 3

INFLUENCE OF TEMPERATURE ON THE RATE OF FORMATION OF DIMETHYLDICHLOROGERMANE

Contact mass type	Cu (%)	Pressure of CH_3Cl (mm)	Temp. (°C)	Rate, W (10^3 mmole·g^{-1}·min^{-1})	Activation energy, E (kcal/mole)
Mixture of powders	27	650	340–365–340	1.4–3.3–1.6	24.4
GeCu alloy	3.0	650	345–375–345	1.6–4.0–1.65	24.5
	13.8	650	350–375–350	1.4–2.9–1.4	24.0
	30	650	345–375–345	1.33–3.9–1.43	27.5
	30	650	350–370–350	1.9–3.75–2.05	27.5

TABLE 4

THE ORDER OF REACTION WITH RESPECT TO RCl IN THE SYNTHESIS OF TRICHLOROGERMANE, TRICHLOROSILANE, DIMETHYLDICHLOROSILANE AND DIMETHYLDICHLOROGERMANE

Compound	Reaction order			Activation energy, E (kcal/mole)			
	Polycryst. Ge or Si[a]	With Cu		Polycryst. Ge or Si[a]	With Cu		
		10–13%	30%		3%	10–13%	30%
$HSiCl_3$[20]	0.0–0.1	0.2–0.4		34.0		23.0	
$(CH_3)_2SiCl_2$[23]		0.9–1.2				29.0	
$HGeCl_3$[23]	0.8–0.9	0.8–0.9	0.8–0.9	23.0	12.0	12.0	12.0
$(CH_3)_2GeCl_2$		1.5	1.5			26.0	26.0

[a] Purity Si: 99.9999%; Ge: 99.999%.

the reaction rate and activation energy are independent of the nature of the contact mass type (powder mixture or alloy) and the quantity of copper.

It is interesting to compare the data with those for formation reactions of trichlorogermane, trichlorosilane and dimethyldichlorosilane. As is seen from Table 4, the reaction order in the trichlorosilane syntheses changes from 0.0–0.1 in absence of copper to 0.4 in its presence, but for the trichlorogermane synthesis it is about 0.9 independent of whether copper is present or not. Because methyl chloride reacts too slowly with silicon and germanium in the absence of copper, the order was not established under such conditions, but in the presence of copper the order is higher for germanium than for silicon.

A characteristic feature of all the reactions included in Table 4 is the strong influence of copper on the activation energy; this is more marked in the reactions with germanium involving the synthesis of trichlorosilane and trichlorogermane. The syntheses from silicon, especially the hydrochlorination involve higher activation energies than those from germanium.

Recent investigations[23] of methyl chloride adsorption on germanium and its alloys with copper shows that rapid and reversible adsorption occurs at temperatures lower than that at which formation of dimethyldichlorogermane begins, so we consider that the methyl chloride adsorption on germanium is mainly molecular rather than dissociative, and so cannot determine the rate of the synthesis.

The mechanism of dimethyldichlorogermane formation more probably involves as the limiting step the surface reaction of chemisorbed molecular methyl chloride. The high values of the reaction order for methyl chloride ($n \simeq 1.5$) in this synthesis, suggest the participation of two CH_3Cl molecules in the activated complex; the activation energy is then determined by the bond energies of the absorbed methyl chloride molecules and the strength of binding of the surface germanium atoms involved in the transition state.

Since the nature of the methyl chloride adsorption does not vary between germanium and its alloys[23] the M–Cl bond energy in the adsorbed molecules is probably little affected by the copper additions. Therefore the main role of copper in the synthesis of dimethyldichlorogermane is to weaken the bond between the germanium atoms.

It is interesting to note that the reaction order in the synthesis of trichlorogermane does not change on introduction of copper, and the main influence is to cause a sharp decrease in the activation energy (Table 4). It is well known that the reaction order for a gaseous reactant in a heterogeneous catalytic reaction is determined by the state of the adsorbate on the surface. With silicon both the order and the activation energy are changed by the addition of copper.

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