

Disproportionation reactions of organohydrosilanes in the presence of base catalysts

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Abstract

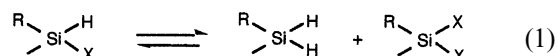
Alkoxides, alkyl compounds, amides and hydrides of alkali metals (M) and barium, such as MOR, Ba(OR)₂, *n*-BuM, PhM, MN(SiMe₃)₂ and MAIH₄ showed high catalytic activities versus the disproportionation reactions of PhSiH₃ to produce SiH₄, Ph₂SiH₂ and Ph₃SiH. A good correlation between the catalyst basicities and the catalytic activities was observed, and a reaction mechanism involving the metal hydride and alkyl metal was proposed. A considerable amount of SiH₄ was produced in the reduction of PhSiCl₃ with LiAlH₄ when over three moles of LiAlH₄ was used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Disproportionation reactions; Phenylsilane; Base catalysts

1. Introduction

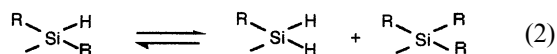
In reactions involving organometallic compounds such as organosilicon compounds, there have been many reports on catalytic reactions using transition metal compounds as catalysts [1,2]. On the other hand, there are few catalytic reactions reported using compounds of the main group elements as catalysts, which are generally ionic compounds, even though ionic catalysts have some industrial advantages, for example they can be easily prepared at low cost and can be separated from the reacted solution using ion-exchange resins or zeolites. We have been studying reaction systems involving organosilicon compounds such as hydrosilanes, using ionic compounds as the catalysts, and have found high catalytic activities of some compounds of alkali and alkaline-earth metals toward the hydrosilylation reactions of hydrosilanes with olefins [3] and dehydrogenative coupling reactions between hydrosilanes and alkynyl compounds [4–8]. In this paper, we report a new catalytic reaction system using ionic compounds as the catalyst.

Catalytic disproportionation reactions of alkoxy silanes and chlorosilanes have been studied by treating such silanes with a suitable catalyst under mild conditions shown as follows (Eq. (1)):

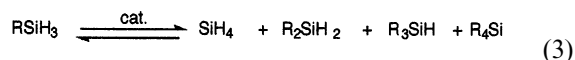


wherein R is a hydrocarbon group or hydrogen, and X is an alkoxy group or halogen [9]. Base catalysts such as alkali metal alkoxides have generally been employed.

There have been some reports on the disproportionation reactions of organohydrosilanes using Lewis acids such as AlBr₃ [10], solid acids such as SiO₂–Al₂O₃ [11], KH, LiAlH₄ [12], Red-Al [13] and transition metal complexes such as (Ph₃P)₃RhCl [14], Cp*Fe₂(CO)₄(μ-CO)(μ-PPh₂) [15], Cp*₂SmCH(SiMe₃)₂ [16] or RuCl₂[P(C₆H₄Me-*p*)₃] [17] (Eq. (2)).



In this paper, we report the disproportionation reactions of arylhydrosilanes in the presence of base catalysts such as alkoxides, alkyl compounds, amides or hydrides of alkali or alkaline earth metals (Eq. (3)).



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2. Experimental

2.1. Reaction procedures

PhSiH₃, Ph₂SiH₂, Ph₃SiH, C₆H₁₃SiH₃ (*n*-hexylsilane) and Et₃SiH were used as the hydrosilanes for the disproportionation reactions. These liquid reactants were dried over 3 Å molecular sieves prior to use. Alkali and alkaline-earth metal compounds were mainly used as the catalysts (see Table 1). The solvents of diglyme, 1,2-dimethoxyethane (DME), THF, 1,4-dioxane, hexane and toluene were dried over 3 Å molecular sieves. All experiments were carried out in a nitrogen atmosphere. A 50 mmol sample of the hydrosilane, 2.5 mmol of the catalyst and 10 ml of the solvent were typically charged into a glass flask which was connected with a condenser cooled to 15°C. The reactions were carried out at 50°C for 6 h. The gaseous products were trapped by reaction with a solution of LiOEt in ethanol (Li 0.5 wt.%). After the reaction, the amounts of liquid products in the reaction solution and the gaseous products trapped as alkoxides in the ethanol solution (the amounts of Si(OEt)₄ and R_nSi(OR)_{4-n}) were determined by GC measurement using *n*-tetradecane as the internal standard.

The reduction of PhSiCl₃ to PhSiH₃ was carried out in THF using LiAlH₄ with specific mole ratios of PhSiCl₃ to LiAlH₄ in a nitrogen atmosphere. Forty

seven ml of THF and 10 mmol of PhSiCl₃ were charged into a 200 ml glass flask with a condenser cooled to 15°C. LiAlH₄ (solution of THF, 2.16 mol l⁻¹) of the specified quantity was then gradually added, while the temperature was maintained at 40°C or less by cooling. After 1 h, the reaction temperature was raised to ca. 65°C, and the reaction mixture was refluxed with stirring for an additional 2 h. The products were analyzed in a manner similar to the disproportionation reaction.

2.2. Product assignment

The liquid products (PhSiH₃, Ph₂SiH₂, Ph₃SiH, Si(OEt)₄) were identified by mass spectroscopy [18] and GC.

PhSiH₃; MS (*m/z*): (EI mode) 108 (100, M⁺), 107 (100), 106 (98), 105 (73), 81 (20).

Ph₂SiH₂; MS (*m/z*): (EI mode) 106 (100), 105 (50), 184 (37, M⁺), 78 (33), 53 (17).

Ph₃SiH; MS (*m/z*): (EI mode) 182 (100), 181 (59), 183 (29), 105 (23), 260 (18, M⁺).

Si(OEt)₄; MS (*m/z*): (EI mode) 193 (100), 149 (86), 163 (70), 79 (57), 208 (11, M⁺).

The gaseous product (SiH₄) was trapped directly in a cylinder and identified by mass spectroscopy.

SiH₄; MS (*m/z*): (EI mode) 30 (100), 31(86), 29 (15), 32 (11, M⁺). The data coincided with those in the literature [18,19].

Table 1
Disproportionation reactions of PhSiH₃^a

Entry	PhSiH ₃ (mmol)	Catalyst	Amount of catalyst (mmol)	Reaction temperature (°C)	Conversion of PhSiH ₃	Product yield (%) ^b			
						SiH ₄	Ph ₂ SiH ₂	Ph ₃ SiH	Ph ₄ Si
1	49.9	LiOEt	2.5	50	32.0	9.8	10.3	0	0
2	50.6	LiO- <i>i</i> -Pr	2.5	50	58.7	17.0	17.4	0	0
3	50.2	LiOPh	2.5	50	0	0	0	0	0
4	50.5	NaOEt	2.5	50	99.3	44.7	2.9	28.0	0.8
5	49.7	KOEt	2.4	50	97.5	50.4	6.9	15.2	7.0
6	50.7	Ba(OC ₈ H ₁₇) ₂ ^c	2.5	50	98.2	25.5	23.0	15.1	0.1
7	50.3	LiOCOPh	2.5	50	0	0	0	0	0
8	50.2	<i>n</i> -BuLi	2.5	50	96.5	43.7	41.3	2.7	0
9	49.8	PhLi	2.5	50	97.3	46.6	38.2	8.4	0
10	49.1	LiN(SiMe ₃) ₂	2.6	50	85.0	36.6	36.9	1.1	0
11	50.7	LiN(SiMe ₃) ₂	2.6	100	99.0	53.1	16.3	21.4	0
12	50.2	NaN(SiMe ₃) ₂	2.5	50	95.4	39.2	34.1	2.0	0.1
13	50.4	KN(SiMe ₃) ₂	2.5	50	96.3	39.7	36.7	1.5	Trace
14	50.4	LiAlH ₄	2.5	50	94.2	47.6	25.8	13.2	0
15	49.4	LiAlH ₄	2.6	100	98.1	57.2	9.3	23.8	0.1
16	50.8	NaAlH ₄	2.5	50	91.0	41.3	30.3	8.5	Trace
17	49.6	MgO ^d	126	50	23.6	1.9	3.3	0	0

^a Reactions were carried out for 6 h. 10 ml of diglyme was used as the solvent unless otherwise noted.

^b Determined by GC.

^c Barium-2-ethylhexoxide.

^d 5.06 g of MgO was used.

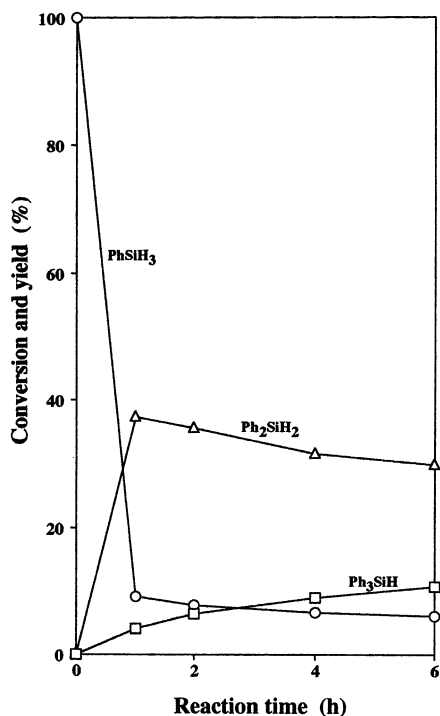


Fig. 1. Disproportionation reaction of PhSiH₃ in the presence of LiAlH₄ (entry no.1 in Table 1).

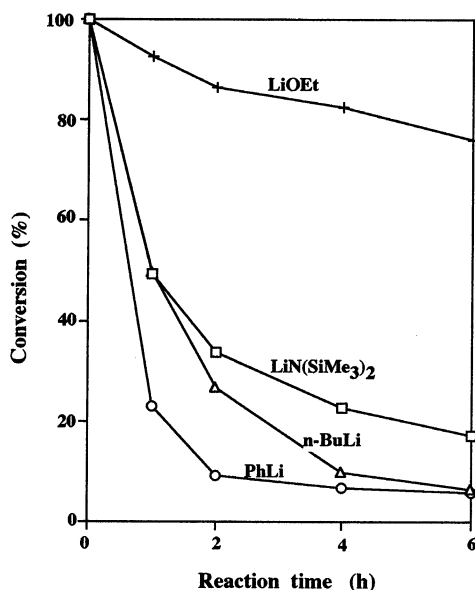


Fig. 2. Disproportionation reaction of PhSiH₃ in the presence of Li compounds.

3. Results and discussion

The reaction results are shown in Table 1. The disproportionation reactions of PhSiH₃ occurred to produce the monosilane (SiH₄), Ph₂SiH₂, Ph₃SiH, and Ph₄Si in the presence of alkoxides, alkyl compounds, amides or hydrides of alkali metals and barium alkoxides, which are strong bases. No other products were

detected by GC. The first reaction of PhSiH₃ proceeded rapidly during the early stages of the reaction with the production of SiH₄, and Ph₂SiH₂, and then the reaction of Ph₂SiH₂ to produce Ph₃SiH gradually proceeded as shown in Fig. 1. Because SiH₄ was identified by conversion to Si(OEt)₄, some SiH₄ would be lost, especially during the early reaction stage. When we did not use the trap containing the ethanol solution of LiOEt, which was connected to the reaction vessel to convert SiH₄ into Si(OEt)₄ with hydrogen gas evolution, smoke or a flame was observed at the exit of the reaction vessel.

The alkoxides of the elements belonging to Groups 2 (alkaline earth metals), 11, 13 and 3 of the periodic table such as Mg(OEt)₂, Ca(OEt)₂, Sr(OEt)₂, Ba(OEt)₂, Cu(OEt)₂, Al(OEt)₃, Ga(OEt)₃ and La(O-*i*-Pr)₃, which have higher ionization potential energies [20] and are weaker bases than the alkali metal alkoxides, were insoluble in the reaction solution and showed almost no catalytic activity. Ba(OC₈H₁₇)₂ (barium-2-ethylhexoxide), which is soluble in the solvent, showed a high catalytic activity.

The order of the catalytic activities of Li compounds was PhLi > *n*-BuLi > LiN(SiMe₃)₂ > LiOEt ≫ LiOPh, LiOCOPh (not catalytically active) as shown in Fig. 2. The order coincides with that of the basicities of the conjugated acids [21]. Moreover, the catalytic activities of the alkali metal alkoxides (NaOEt ~ KOEt > UOEt) correlate with the ionization potentials of the metals (see Table 1, Fig. 3) [20]. Because the alkali compounds were soluble in the reaction solution, the basicity of the catalyst would be one of the factors which determines the catalytic activity. The addition of 10% of a more

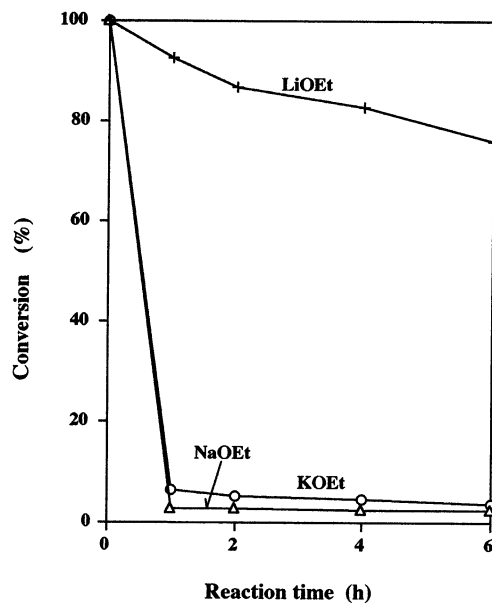


Fig. 3. Disproportionation reaction of PhSiH₃ in the presence of alkali metal alkoxide.

Table 2

Effects of solvent and catalyst amount on disproportionation reaction of PhSiH_3 in the presence of NaOEt^a

Entry	PhSiH_3 (mmol)	NaOEt (mmol)	Solvent ^b	Conversion of PhSiH_3	Product yield (%) ^c			
					SiH_4	Ph_2SiH_2	Ph_3SiH	Ph_4Si
1	50.5	2.5	Diglyme	99.3	44.7	2.9	28.0	0.9
2	50.0	2.5	DME	99.6	53.7	2.4	28.5	1.2
3	50.6	1.3	DME	99.7	52.1	4.3	28.2	0.2
4	50.5	0.3	DME	50.0	17.2	20.9	0.1	0
5	50.5	2.5	THF	99.9	53.7	4.8	26.6	0.2
6	49.8	2.5	1,4-Dioxane	30.5	8.7	9.6	0	0
7	50.5	2.5	Hexane	0	0	0	0	0
8	50.5	2.5	Hexane–diglyme ^d	98.0	46.0	28.4	13.5	0
9	50.7	2.4	Toluene	0	0	0	0	0
10	50.0	2.5	Toluene–diglyme ^e	97.4	47.1	33.3	10.4	0

^a Reactions were carried out at 50°C for 6 h.^b 10 ml of the solvent was used unless otherwise noted.^c Determined by GC.^d 10 ml of hexane and 1 ml of diglyme were used.^e 10 ml of toluene and 1 ml of diglyme were used.

polar solvent to a non-polar solvent yields results analogous to those in the polar solvent alone (Table 2). This might suggest that there is preferential solvation of the transition state with the more polar solvent.

The reaction mechanism in which the substituent moves from the silicon to the lithium is considered ($\text{Si}\cdots\text{H}\cdots\text{Li}$, see Fig. 4). When the substituent is a phenyl group, the activation energy would be low due to the resonance effect of the benzene ring and the reaction would proceed easily. $\text{C}_6\text{H}_{13}\text{SiH}_3$ was not disproportionated. There would be no resonance effect in alkyl substitution. The conversion of Et_3SiH was zero and that of Ph_3SiH was much lower than that of PhSiH_3 , which would be caused by steric hindrances (Table 3).

As mentioned above, the strong basic catalysts showed high catalytic activities. We presumed that the reaction proceeded via an ionic transition state as shown in Fig. 4. It is well known that alkyl metals [22], metal amides [23] and metal alkoxides [23,24] react with PhSiH_3 to produce metal hydrides [22]. PhSiH_3 would be activated by the alkyl metal and metal hydride and a disproportionation reaction would occur. We proposed the four-center-type transition state as shown in Fig. 4. Five-coordinate silicon hydrides could also be considered as an intermediate [12,25]. More study must be done to clarify the reaction mechanism. The above results indicate that the Si–H bond would be more easily activated by an ionic catalyst than the C–H bond, because the C–H bond cannot generally be activated by base catalysts such as alkoxides, alkyl compounds, amides or hydrides of alkali metals.

The fact that LiMH_4 catalyzed the disproportionation reaction of organohydrosilane to produce SiH_4 is very important, because almost all organohydrosilanes are usually synthesized by the reduction of the corre-

sponding organochlorosilanes [26], which are easily obtained by Rochow's direct process via the reaction of RCl with silicon metal.

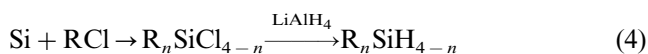


Fig. 5 shows the amount of SiH_4 produced during the reduction of PhSiCl_3 with LiAlH_4 for various ratios of LiAlH_4 to PhSiCl_3 . A considerable amount of SiH_4 was produced when over 3 mol of LiAlH_4 was used.

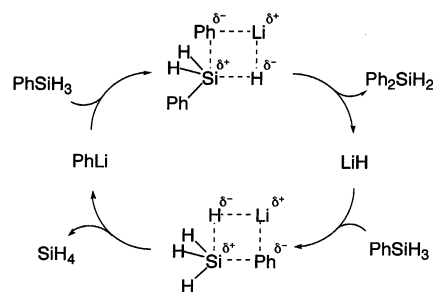


Fig. 4. Presumed mechanism of the disproportionation reaction of hydrosilane in the presence of alkali metal compound.

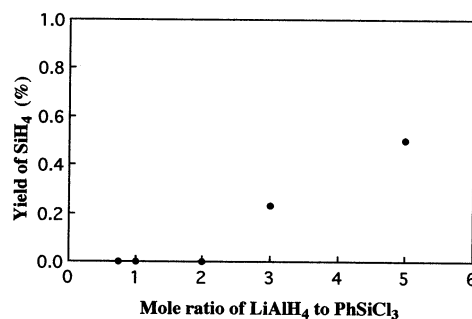


Fig. 5. The amount of SiH_4 produced in the reduction of PhSiH_3 by LiAlH_4 .

Table 3
Disproportionation reaction of hydrosilanes in the presence of NaOEt ^a

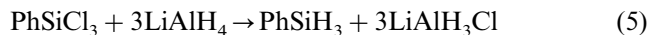
Entry	Hydrosilane	Amount of hydrosilane (mmol)	NaOEt (mmol)	Solvent ^b	Conversion of hydrosilane (%)	Product yield (%) ^c				
						SiH ₄	RSiH ₃	R ₂ SiH ₂	R ₃ SiH	R ₄ Si
1	PhSiH ₃	50.1	0.5	DME	97.8	47.5		27.1	13.0	0
2	Ph ₂ SiH ₂	50.0	0.50	DME	82.9	20.2	0.6		51.7	0.1
3	Ph ₃ SiH	50.0	0.49	DME	7.9	0.2	0	0		1.0
4	C ₆ H ₁₃ SiH ₃	48.9	0.50	DME	0	0		0	0	0
5	PhSiH ₃	50.5	2.5	Diglyme	99.3	44.7	0.7	2.9	28.0	0.9
6	C ₆ H ₁₃ SiH ₃	49.1	2.39	Diglyme	0	0		0	0	0
7	Et ₃ SiH	49.4	2.82	Diglyme	0	0	0	0		0

^a Reactions were carried out at 50°C for 6 h.

^b 10 ml of the solvent was used unless otherwise noted.

^c Determined by GC.

The mole ratio of $\text{LiAlH}_4/\text{PhSiCl}_3$, which gave SiH_4 , suggests that the partially chlorinated aluminum hydrides such as LiAlH_3Cl or $\text{LiAlH}_2\text{Cl}_2$ would not be as active as LiAlH_4 for the disproportionation reaction of PhSiH_3 .



These results caution us that there is the possibility of the generation of SiH_4 (self-burning gas in air, minimum explosion limit is 0.8 vol%) during the reduction of PhSiCl_3 by LiAlH_4 . Because the reaction solution is not always homogeneous, we must take sufficient care, especially when we use an amount of LiAlH_4 larger than the equivalent amount of an organochlorosilane.

4. Conclusions

Alkoxides, alkyl compounds, amides and hydrides of alkali metals (M) and barium, such as MOEt , $\text{MO-}i\text{-Pr}$, $\text{Ba}(\text{OC}_8\text{H}_{17})_2$, $n\text{-BuM}$, PhM , $\text{MN}(\text{SiMe}_3)_2$ and MAIH_4 (M; Li, Na, K) showed high catalytic activities for the disproportionation reactions of PhSiH_3 to produce SiH_4 , Ph_2SiH_2 and Ph_3SiH . Hydrosilanes having alkyl substitutions, such as $\text{C}_6\text{H}_{13}\text{SiH}_3$ (n -hexylsilane) and Et_3SiH were not disproportionated. The catalytic activities have good correlation with the ionization potentials of the metals and the $\text{p}K_{\text{a}}$ of the conjugated acids of the catalysts. An ionic reaction mechanism involving the metal hydride and alkyl metal was proposed. A considerable amount of SiH_4 was produced in the reduction of PhSiCl_3 with LiAlH_4 when over 3 mol of LiAlH_4 were used.

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