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An Examination of the Chlorination of Silanes by Silver Chloride

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It has been demonstrated that the relative rates of chlorination with AgCl follow the order $Si_2H_6 \gg CH_3SiH_3 > SiH_4 > ClSiH_3$. A mechanism has been suggested which will explain this order. The reaction with $CH_3Si_2H_5$ has generated $CH_3ClSiHSiH_3$, $CH_3SiH_2SiH_2Cl$, $CH_3(Cl)SiHSiH_2Cl$, and $CH_3(Cl)SiHSiHCl_2$, while $CH_3SiCl_2SiH_3$ has been obtained by rearrangement reactions over Al_2Cl_6. The formation of the first four compounds has been discussed in terms of steric and inductive effects.

The halogenation of germane,[1] digermane,[1] silane,[2] alkylsilanes,[2] and disilane[2,3] by silver chloride or silver bromide has demonstrated that these gas–solid reactions can be very useful. To date, the results reported have centered on the preparation of new compounds or on new procedures for the preparation of previously reported compounds. In this article, we report our results on an investigation aimed at obtaining some understanding about the reaction between silicon–hydrogen bonds and silver chloride.

Results and Discussion

1. Reaction of AgCl with Monosilanes and Disilane.

—The results of the reaction between AgCl and CH_3SiH_3, SiH_4, and $ClSiH_3$ at 236° are listed in Table I.

TABLE I

REACTION OF AgCl WITH SiH_4, CH_3SiH_3 AND $ClSiH_3$[a]

Reactant	Vapor pressure, mm	Amt of chlorinated product (normalized),[b] mmol	Reactant	Vapor pressure, mm	Amt of chlorinated product (normalized),[b] mmol
SiH_4	11	0.57[c]	$ClSiH_3$	12	0.28[e]
$ClSiH_3$	12	0.29[e]	CH_3SiH_3	13	1.2[f]
CH_3SiH_3	13	1.0[f]	SiH_4	11	0.70
SiH_4	11	0.75[d]			

[a] All reactions at 236° for 12 min conducted sequentially over the same AgCl. [b] Normalized to 11 mm pressure, *i.e.*, multiplied by $^{11}/_{12}$($ClSiH_3$) or $^{11}/_{13}$(CH_3SiH_3). [c] $ClSiH_3$ (0.49 mmol) and Cl_2SiH_2 (0.08 mmol). [d] $ClSiH_3$ (0.60 mmol) and Cl_2SiH_2 (0.15 mmol). [e] Cl_2SiH_2 and a trace of Cl_3SiH. [f] CH_3SiH_2Cl and a trace of CH_3SiHCl_2.

The runs are listed sequentially over the same AgCl. Thus, each run was carried out over slightly less AgCl but more silver. The reactions were carried out in a recirculating flow system which contained a cold trap which set the reactant pressure and condensed the chlorinated products. Since we assumed that these reactions are first order in the silane pressure, we have normalized the product yields to 11 mm pressure. The data in Table I demonstrate that the rate of reaction with AgCl is $CH_3SiH_3 > SiH_4 > ClSiH_3$. Since the AgCl was being used, one would expect a decrease in yields with each run. The slight increase noted may be due to some catalysis from the silver being generated.

An examination of the data reported for the reaction of AgCl with SiH_4[2,3] and Si_2H_6[2,3] or GeH_4[1] and Ge_2H_6[1] strongly suggests that Si_2H_6 (Ge_2H_6) is more reactive toward AgCl than SiH_4 (GeH_4). However, data are reported at different temperatures. In Table II we report results of the reaction of AgCl with Si_2H_6 and SiH_4 which clearly show that the rate of reaction with Si_2H_6 is greater than with SiH_4.

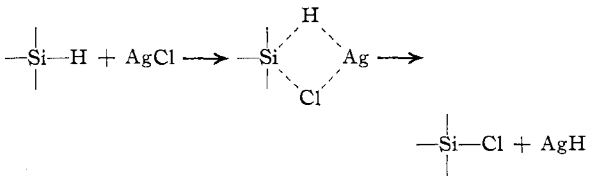
TABLE II

REACTION OF AgCl WITH Si_2H_6 AND SiH_4

Temp, °C		Amt of reactant, mmol Used	Amt of reactant, mmol Consumed	Products	Amt of products, mmol
22.5	Si_2H_6	0.74	0.28	$ClSi_2H_5$ 1,1- and 1,2-$Cl_2Si_2H_4$ 1,1,2-$Cl_3Si_2H_3$	0.28
22.5	SiH_4	0.74	0.026	$ClSiH_3$ $Cl_2Si_2H_2$[a]	0.026
106	SiH_4	0.71	0.13	$ClSiH_3$ Cl_2SiH_2[a]	0.13
				HCl	0.043

[a] Minor component.

Combining these results, we have that the rate of reaction with AgCl is in the order $Si_2H_6 \gg CH_3SiH_3 > SiH_4 > ClSiH_3$. The observed order for the last three compounds suggests that the more hydridic the hydrogen, the more favored is the reduction. The fact that Si_2H_6 is so much more reactive than SiH_4 cannot be explained by a great increase in hydridic character for the disilane hydrogen atoms. However, the increase in rate could be accounted for by the formation of a four-centered intermediate if disilane is a stronger Lewis acid than SiH_4 (eq 1). The increased Lewis acidity of a disilane over a silane has been demonstrated kinetically with $(CH_3)_3SiH$ and $(CH_3)_5Si_2H$[4] and in a $-Si_2H_5$ group over a $-SiH_3$ group.[5] This increase in acidity is presumably due to $d\pi$–$d\pi$ overlap in the silicon–silicon bond of the disilane in the transition state during nucleophilic substitution.


(1)

The relative stabilities for the formation of complexes as in eq 1 would be determined by the strength of the Si---Cl and the Ag---H interactions. For the monosilanes, the Ag---H interaction expected would be $CH_3SiH_3 > SiH_4 > ClSiH_3$; while the opposite order would be expected for the Si---Cl interaction. Thus the observed results should be due to the differences of these

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(1) K. M. MacKay, P. Robinson, E. J. Spanier, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **28**, 1377 (1966).

(2) R. P. Hollandsworth, W. M. Ingle, and M. A. Ring, *Inorg. Chem.*, **6**, 844 (1967).

(3) R. P. Hollandsworth and M. A. Ring, *ibid.*, **7**, 1635 (1968).

(4) F. K. Cartledge, *J. Organometal. Chem.*, **13**, 516 (1968).

(5) C. H. VanDyke and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 747 (1964).

interactions. For Si_2H_6, the Si---Cl interaction should be relatively strong and the Ag---H interaction could be as strong or stronger than that in CH_3SiH_3. These additive effects could explain the high relative rate for the reaction with Si_2H_6.

2. Reaction of AgCl with Methyldisilane.—The reaction between AgCl and $CH_3Si_2H_5$ was carried out at 0° in a recirculating flow system with a low-temperature trap. In this system, the monochloro derivatives obtained were $CH_3SiH_2SiH_2Cl$ and $CH_3(Cl)SiHSiH_3$ in a ratio of 4.1 ± 0.3, while the di- and trichloro derivatives obtained were $CH_3(Cl)SiHSiH_2Cl$ and $CH_3(Cl)SiHSiHCl_2$.

When the reaction between AgCl and $CH_3Si_2H_5$ was carried out in an essentially static system (reaction time 1 min) at 50°, the monochloro derivatives obtained were $CH_3SiH_2SiH_2Cl$ and $CH_3(Cl)SiHSiH_3$ in a ratio of about 2:1, respectively. The same di- and trichloro derivatives were obtained. The change in the ratio of the monochloromethyldisilanes suggests that conversion of $CH_3SiH_2SiH_2Cl$ to $CH_3(Cl)SiHSiH_3$ occurs during the chlorination. In section 4, we report results of disproportionation reactions which further support this contention. These data allow us to report the following reactions: sequence A (where the ratio of route 2 to route 3 is $\gtrsim 4$)

$$CH_3Si_2H_5 + AgCl \longrightarrow CH_3SiH_2SiH_2Cl + 0.5H_2 + Ag \qquad (2)$$

$$CH_3Si_2H_5 + AgCl \longrightarrow CH_3(Cl)SiHSiH_3 + 0.5H_2 + Ag \qquad (3)$$

and sequence B

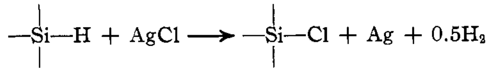
$$CH_3SiH_2SiH_2Cl + AgCl \longrightarrow CH_3(Cl)SiHSiH_2Cl + 0.5H_2 + Ag \qquad (4)$$

$$CH_3(Cl)SiHSiH_3 + AgCl \longrightarrow CH_3(Cl)SiHSiH_2Cl + 0.5H_2 + Ag \qquad (5)$$

$$CH_3(Cl)SiHSiH_2Cl + AgCl \longrightarrow CH_3(Cl)SiHSiHCl_2 + 0.5H_2 + Ag \qquad (6)$$

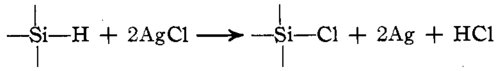
The results reported as eq 2–6 can be explained by steric effects (eq 2 *vs.* eq 3; eq 5 and 6) and by inductive effects (eq 4). The results from the reaction of AgCl with monosilanes would indicate that reaction 3 should be favored over reaction 2. However, the α silicon is much more sterically hindered and thus halogenation occurs primarily on the β silicon. The two silicon atoms in $CH_3SiH_2SiH_2Cl$ are sterically similar and the halogenation was inductively controlled as the only observed product was $CH_3(Cl)SiHSiH_2Cl$. The halogenations in reactions 5 and 6 were sterically controlled.

It was noted that the reaction of AgCl with $CH_3Si_2H_5$ at 0° can be represented by eq 7 while the reaction of



$$-\overset{|}{\underset{|}{Si}}-H + AgCl \longrightarrow -\overset{|}{\underset{|}{Si}}-Cl + Ag + 0.5H_2 \qquad (7)$$

monosilanes and AgCl at 236° can be represented by eq 8. This result is in agreement with the earlier results with silanes.[2,3] It is known that AgCl and H_2 react at elevated temperature.[6] Since the hydrogen was



$$-\overset{|}{\underset{|}{Si}}-H + 2AgCl \longrightarrow -\overset{|}{\underset{|}{Si}}-Cl + 2Ag + HCl \qquad (8)$$

$$AgCl + 0.5H_2 \longrightarrow Ag + HCl \qquad (9)$$

contained in our system, the change in product (H_2 *vs.* HCl) with temperature can be explained. The hydrogen produced from the AgCl chlorination of GeH_4 at 260° was pumped off[1] so that it is reasonable that step 9 was not observed.

3. Reaction of HCl with Methyldisilane.—The monochlorinated methyldisilanes obtained from the Al_2Cl_6-catalyzed reaction of HCl with $CH_3Si_2H_5$ were $CH_3ClSiHSiH_3$ and $CH_3SiH_2SiH_2Cl$ in a ratio of 2.5:1.

4. Rearrangement Reactions over Aluminum Chloride.—Disproportionation reactions of halosilanes are well known and disproportionation of monohalodisilanes over an aluminum halide catalyst have been observed.[7,8]

In Table III we list some preliminary results from disproportionation reactions which are consistent with our contention that $CH_3SiH_2SiH_2Cl$ can be catalytically converted to $CH_3(Cl)SiHSiH_3$ and other compounds.

TABLE III

REACTIONS OVER ALUMINUM CHLORIDE (31°)

	Reactants	Amt, mole fraction	Products	Amt, mole fraction	Time, min
1.	$CH_3ClSiHSiH_3$	0.53	$CH_3SiCl_2SiH_3$	0.35	35
	$CH_3SiH_2SiH_2Cl$	0.47	$CH_3Si_2H_5$	0.35	
			$CH_3(Cl)SiHSiH_3$	0.25	
			$CH_3SiH_2SiH_2Cl$	0.05	
2.	$CH_3ClSiHSiH_2Cl$	0.52	$CH_3SiCl_2SiH_3$	0.76	90
	$CH_3(Cl)SiHSiHCl_2$	0.22	$CH_3(Cl)SiHSiH_3$	0.18	
	$CH_3SiH_2SiH_2Cl$	0.21	$CH_3(Cl)SiHSiH_2Cl$	0.06	
	$CH_3(Cl)SiHSiH_3$	0.05			
3.	1,2-$Cl_2Si_2H_4$	0.9	1,1-$Cl_2Si_2H_4$	0.8	60
	1,1-$Cl_2Si_2H_4$	0.1	$ClSi_2H_5$	<0.1	
			1,2-$Cl_2Si_2H_4$	<0.1	
			1,1,2-$Cl_3Si_2H_3$	<0.1	

Rearrangements were also observed in the mass spectrometer. As seen in Table IV, the mass spectrum of $CH_3(Cl)SiHSiH_2Cl$ had fairly intense peaks due to the $CH_3SiCl_2^+$ and it would appear that $CH_3SiH_2SiH_2Cl$ also yielded the $CH_3(Cl)SiH^+$ and the CH_3SiCl^+ ions. We have observed this type of rearrangement earlier in 1,2-$Cl_2Si_2H_4$[3] when peaks due to $SiCl_2^+$ and $HSiCl_2^+$ were observed.

TABLE IV

SOME MASS SPECTRAL DATA OF CHLORINATED METHYLDISILANES

Compound	Ionization potential, V	Rel intens Parent ion	 $CH_3SiCl_2^+$	 CH_3SiClH^+ + CH_3SiCl^+
$CH_3(Cl)SiHSiH_3$ (20%) + $CH_3SiH_2SiH_2Cl$ (80%)	15	100	...	221
$CH_3(Cl)SiHSiH_2Cl$	10	100	37	142
$CH_3SiCl_2SiH_3$	10	100	47	87

Experimental Section

All reactions and separations were carried out in a standard high-vacuum system. The separations were made by repeated trap to trap distillations through or from low-temperature slush baths as listed. Infrared spectra were obtained in the gas phase on a Perkin-Elmer Model 337 spectrometer. A Varian A-60 spectrometer was used to obtain proton nmr spectra in CCl_4 which are reported relative to TMS at δ 0.00 as an internal standard. Mass spectra were obtained on a Hitachi RMU-6E spectrometer.

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(6) A. Van Tiggelen, L. Vanreusel, and P. Neven, *Bull. Soc. Chim. Belg.*, **61**, 651 (1952).

(7) L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **20**, 345 (1961).

(8) A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962).

Silane, Si_2H_6, and CH_3SiH_3 were obtained from the $LiAlH_4$ reduction of the corresponding chloro compounds. Chlorosilane was obtained from the reaction of SiH_4 with $AgCl_2$.[2] These compounds were identified spectroscopically. Their infrared spectra were identical with those reported[9] while their mass spectra contained no ions of greater mass than the molecular weight with ^{30}Si present. The absence of the very strong 910-cm^{-1} band of SiH_4 from the infrared spectra of Si_2H_6, CH_3SiH_3, and $ClSiH_3$ demonstrated that it was not present in these samples.

Methyldisilane was obtained from the copyrolysis of Si_2H_6 and CH_3SiH_3[10] with a −78° bath in place of the −95° bath. Methyldisilane was identified by an infrared and a mass spectrum.[11] The absence of Si_2H_6 was demonstrated by the fact that the mass spectral peak at *m/e* 62 was virtually absent while Si_2H_6 has a very intense peak at *m/e* 62.[12]

The flow reaction vessel used for the reactions of AgCl with SiH_4, $ClSiH_3$, and CH_3SiH_3 at 236° and with $CH_3Si_2H_5$ at 0° consisted of a 25-mm Pyrex tube with a test tube end. A centered 10-mm tube was inserted through the side and open near the bottom of the larger tube. Glass wool with AgCl was packed around the 10-mm tube. The top end of the 25-mm tube led to two "U" low-temperature traps which were connected *via* an automatic Toepler pump to the 10-mm tube. The 25-mm tube was heated with a heating tape or cooled with an ice bath. Temperatures were measured with a thermometer in contact with the outer tube.

1. **Reaction of AgCl with Monosilanes and Disilane. A. Reaction at 236° with Monosilanes.**—The results of the experiments listed in Table I were carried out in the reactor described above which was charged with 20.9 mmol of AgCl. The salt was dried at 240° under dynamic vacuum for 3 days. The silane, about 2 mmol, was condensed into the reaction system. The "U" traps were cooled to −160° for the reactions with SiH_4, to −95° for the reactions with $ClSiH_3$, and to −112° for the reactions with CH_3SiH_3. After 12 min of cycling through the heated AgCl, the mixtures were analyzed.

The volatile fraction from the reaction with SiH_4 was passed through baths cooled to −196, −160, −130, and −112°. The fraction passing −196° was H_2 while the condensate in the −196° trap was SiH_4 (identified as described earlier). The product condensed at −112° was Cl_2SiH_2 identified by an infrared spectrum[13] and a mass spectrum. The condensate in the −130° trap was a mixture of $ClSiH_3$ and Cl_2SiH_2 in about a 9:1 ratio as determined by infrared and mass spectra. The condensate in the −160° trap was a mixture of HCl and $ClSiH_3$ in about a 19:1 ratio as determined by infrared and mass spectra. The product quantities listed in Table I ($ClSiH_3 + Cl_2SiH_2$) were obtained by adding the products condensed at −112 and −130° and the appropriate fraction condensed at −160°. This quantity was compared to the amount of SiH_4 consumed and also compared to the amount of $ClSiH_3 + Cl_2SiH_2$ determined as follows [$Q(\mathrm{A})$ = quantity of A]: $Q(ClSiH_3) + 2Q(Cl_2SiH_2) = \text{final } Q(SiH_4) + Q(ClSiH_3 + Cl_2SiH_2 + HCl) + 2Q(H_2) - \text{initial } Q(SiH_4)$. The quantity [final $Q(SiH_4) + Q(ClSiH_3 + Cl_2SiH_2 + HCl)$] was the total amount of condensate in the −196, −160, −130, and −112° traps. The precision of the three methods was 5%.

The volatile fraction from the AgCl reaction with $ClSiH_3$ was passed through baths of −196, −130, and −112°. Hydrogen passed the −196° trap while the condensate at −196° was a mixture of HCl and $ClSiH_3$. The condensate in the −130° trap was $ClSiH_3$ and Cl_2SiH_2 while the condensate in the −112° trap was Cl_2SiH_2 with only a trace of Cl_3SiH. These fractions were identified as described above. Since very little Cl_3SiH was obtained, the quantity of Cl_2SiH_2 produced could easily be determined from the equation

$$Q(Cl_2SiH_2) = \text{final } Q(ClSiH_3) + Q(Cl_2SiH_2 + HCl) + 2Q(H_2) - \text{ initial } Q(ClSiH_3)$$

This quantity of Cl_2SiH_2 was compared to the Cl_2SiH_2 in the −112° trap and the small quantity estimated present in the −130° trap. These two methods were in good agreement. Since the reaction with $ClSiH_3$ was carried out at 12 mm pressure, the quantity of Cl_2SiH_2 listed in Table I is $^{11}/_{12}$ of that obtained.

The volatile fraction obtained from the AgCl reaction with CH_3SiH_3 was distilled through traps cooled to −196 and −119°. The condensate in the −119° trap was CH_3SiH_2Cl with some CH_3SiH_3 and very little CH_3SiHCl_2. The CH_3SiH_2Cl was identified by an infrared[14] and a mass spectrum. The quantity of CH_3SiH_2Cl produced was determined as

$$Q(CH_3SiH_2Cl) = \text{final } Q(CH_3SiH_3) + Q(CH_3SiH_2Cl + HCl) + 2Q(H_2) - \text{initial } Q(CHSiH_3)$$

This quantity was about 10% less than the amount condensed at −119°. Since some CH_3SiH_3 was in the fraction condensed at −119°, these determinations are in fair accord. The quantity listed in Table I is $^{11}/_{13}$ of the quantity of CH_3SiH_2Cl produced since the pressure of CH_3SiH_3 was 13 mm compared to 11 mm for SiH_4.

B. Single-Pass Reactions with Si_2H_6 and SiH_4.—Single-pass reactions between Si_2H_6 or SiH_4 with AgCl were carried out in a Pyrex tube (2.5 × 38 cm) which was connected to the vacuum system through a ground joint and a three-way stopcock. One lower arm of the stopcock led to the bottom of the Pyrex tube while the other lower arm led from the top of the tube. The AgCl (8.7 g) was held in layers by glass wool. The region containing the AgCl was heated by a heating tape which surrounded a thermometer placed between the tape and tube.

The results listed in Table II were obtained by condensing the volatile reactant in the bottom of the tube (bypassing the AgCl) at −196°. The three-way stopcock was closed and the liquid nitrogen bath removed. After 15 sec, the three-way stopcock was opened and the volatile reactants were distilled through the AgCl layers into the vacuum system. This process was repeated a second time.

For the first listing in Table II, the volatile fraction was distilled through a trap cooled to −95°. The fraction passing the −95° bath was identified as Si_2H_6 by an infrared spectrum which demonstrated that SiH_4 and all chloro compounds (no Si–Cl stretching frequency) were absent. The fraction condensed at −95° had a vapor pressure of 0 mm at −95° and was identified as a mixture of chlorodisilanes by its infrared spectrum.[3]

For the second and third listing in Table II, the volatile fraction was distilled through a trap cooled to −160°. The fraction passing a −160° trap was identified as SiH_4 by an infrared spectrum while the fraction condensing at −160° was identified by an infrared spectrum as a mixture of $ClSiH_3$ and Cl_2SiH_2. In the SiH_4 reaction carried out at 106°, the final volatile fraction condensed at −196° exceeded the initial quantity of SiH_4. This excess was assumed to be a measure of the HCl produced.

2. **Reaction of AgCl with $CH_3Si_2H_5$. A. Preparation of $CH_3(Cl)SiHSiH_3$, $CH_3SiH_2SiH_2Cl$, and $CH_3(Cl)SiHSiH_2Cl$.**— In a typical experiment, $CH_3Si_2H_5$ (1.29 mmol) was passed over 2 g of AgCl for 4.5 hr with the reaction vessel maintained at 0° and the traps cooled to −78°. The product passing a −196° bath was hydrogen (0.75 mmol) identified by a mass spectrum. The condensate in the −196° trap was HCl (0.02 mmol) identified by an infrared spectrum. The absence of absorptions in the C–H and Si–H regions demonstrated the absence of other compounds. The condensate in the −78° trap (0.51 mmol) was a mixture of methylchlorodisilane as identified in section 2B while the condensate in the −55° bath was 0.45 mmol of 1,2-dichloro-1-methyldisilane identified in section 2D. An nmr spectrum of the condensate in the −55° bath demonstrated that 1,2,2-trichloro-1-methyldisilane was absent.

B. Identification of $H_3CSiH_2SiH_2Cl$ and $H_3C(Cl)SiHSiH_3$.— The mixture of monochloromethyldisilanes was identified as follows. (1) The proton nmr absorbances of the two isomers were completely separated except near δ 4.9. The spectrum of $CH_3SiH_2SiH_2Cl$ consisted of a $-CH_3$ triplet at δ 0.38 (J = 4.6 Hz), a $-SiH_2Cl$ triplet at δ 4.83 (J = 2.2 Hz), and a methyl SiH_2- multiplet at δ 3.76. The proton spectrum of $CH_3(Cl)SiHSiH_3$ consisted of a $-CH_3$ doublet at δ 0.74 (J = 4.2 Hz), a $-SiH_3$ doublet at δ 3.38 (J = 2.3 Hz), and a methyl $SiCl-$ broad resonance at about δ 4.90. The relative integrated intensities of the resonances at δ 4.83 and 3.76 were identical which demonstrated that

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[9] J. H. Meal and M. K. Wilson, *J. Chem. Phys.*, **24**, 385 (1956); G. W. Bethke and M. K. Wilson, *ibid.*, **26**, 1107 (1957); S. Kage and S. Tannenbaum, *J. Org. Chem.*, **18**, 1750 (1963); C. Newman, J. K. O. Loane, S. R. Polo, and M. K. Wilson, *J. Chem. Phys.*, **25**, 855 (1956).

[10] P. Estacio, M. D. Sefcik, E. K. Chan, and M. A. Ring, *Inorg. Chem.*, **9**, 1068 (1970).

[11] M. Abedini and A. G. MacDiarmid, *ibid.*, **5**, 2040 (1966).

[12] M. A. Ring, G. D. Beverly, F. H. Koester, and R. P. Hollandsworth, *ibid.*, **8**, 2033 (1969).

[13] D. H. Christensen and O. F. Nielsen, *J. Mol. Spectrosc.*, **27**, 489 (1968).

[14] E. A. V. Ebsworth, M. Onyszchuk, and N. Sheppard, *J. Chem. Soc.*, 1453 (1958).

$CH_3Si_2H_5$[11] was absent. This nmr spectrum also demonstrated that CH_3SiHCl_2[15] was absent.

(2) The mass spectrum at 15 V of a mixture (80%) of $CH_3SiH_2SiH_2Cl$ (analyzed as described in section 1C) consisted of the following heavy-atom envelopes: $CClSi_2H_x^+$ (67.5), $ClSi_2H_x^+$ (7.8), $CClSiH_x^+$ (100.0), $CSi_2H_x^+$ (2.5), $SiCl^+$ (0.9), $Si_2H_x^+$ (1.2), $CSiH_x^+$ (21.9), and HCl^+ (1.8).

The third most intense peak (relative intensity 89 *vs.* 100) was *m/e* 110, which was primarily due to the parent ion $CH_3Si_2H_4{}^{35}Cl^+$. The intensity of the peak at *m/e* 112 ($CH_3Si_2H_4{}^{37}Cl^+$) was 0.36 (calcd 0.38, with 0.05 from ^{30}Si) as intense as the peak at *m/e* 110. The mass spectrum demonstrated that all methyldichlorodisilanes, chlorodisilanes, chlorosilanes, and CH_3SiCl_3 were absent. The infrared spectra reported in Table V for the two monochloromethyldisilanes were obtained from an examination of mixtures of these compounds which varied from 4:1 to 1:8.

TABLE V

INFRARED SPECTRA OF CHLORINATED METHYLDISILANES (CM^{-1})

$CH_3(Cl)$-$SiHSiH_3$	CH_3SiH_2-SiH_2Cl	$CH_3(Cl)$-$SiHSiH_2Cl$	$CH_3SiCl_2SiH_3$	$CH_3(Cl)$-$SiHSiHCl_2$
2960 w	2960 w	2965 w	2965 w	2960 w
2150 vs	2150 vs	2160 vs	2160 vs	2160 vs
1262 m	1262 m	1255 m	1262 s	1262 m
930 s	942 s	932 s	930 s	932[a]
865 s	878 s	880 s	878 vs	880 s
802 vs	798 vs	835 m	790 vs	830 m
730 s	735 m	780 vs	732 s	780 s
538[a]	710 m	740 m	562 s	742 vs
515[b]	538 s	662 w	532 s	650 m
		525 s		574 s
				515 s

[a] Uncertain. [b] Intensity uncertain.

C. **Analysis of Methylchlorodisilane Mixtures.**—The methylchlorodisilane mixtures were analyzed from their nmr spectra. The relative intensities at δ 0.38 and 0.74 were compared on a 1:1 basis while the relative intensities at δ 3.76/2 and 3.38/3 were also compared on a 1:1 basis. These spectral analyses demonstrated that in our flow reactions the ratio of $CH_3SiH_2SiH_2Cl$ to $(CH_3)(Cl)SiHSiH_3$ produced was 4.1 ± 0.3.

D. **Identification of 1,2-Dichloro-1-methyldisilane.**—The identification of 1,2-dichloro-1-methyldisilane was based on the following analyses. (1) The mass spectrum at 10 V consisted of the following heavy-atom envelopes: $Cl_2Si_2CH_x^+$ (100.0), $Cl_2SiCH_x^+$ (31.3), $ClSi_2CH_x$ (3.6), Cl_2SiH^+ (5.7), and $ClSiH_x^+$ (91.5). The most intense peak was at *m/e* 144, which was primarily from the parent ion ($CH_3Si_2H_3{}^{35}Cl_2^+$). The intensity at *m/e* 146, which was primarily due to $CH_3Si_2H_3{}^{35}Cl^{37}Cl^+$, was 0.71 (calcd 0.72, with 0.06 from ^{30}Si) as intense as the peak at *m/e* 144. The intensity at *m/e* 148, which was primarily due to $CH_3Si_2H_3{}^{37}Cl_2^+$, was 0.18 (calcd 0.15, with 0.04 from ^{30}Si) as intense as the peak at *m/e* 144. This mass spectrum demonstrated that trichloromethyldisilanes, polychlorodisilanes, and chlorosilanes were absent.

(2) The nmr spectrum consisted of a $-CH_3$ doublet centered at δ 0.80 (J = 4.1 Hz), a $-ClSiH_2$ doublet centered at δ 5.08 (J = 2.2 Hz), and a $-CH_3(Cl)SiH$ multiplet centered at δ 4.87. This nmr spectrum demonstrated that 1,1-dichloro-1-methyldisilane, both monochloromethyldisilanes, 1,2,2-trichloro-1-methyldisilane, methyldisilane,[11] methyldichlorosilane,[15] and methyltrichlorosilane[16] were absent. The compound 1,1-dichloro-2-methyldisilane was absent since no proton resonances were observed between δ 3.00 and 4.00 or above δ 5.50 as would be expected for this disilane.

E. **Preparation of 1,2,2-Trichloro-1-methyldisilane.**—When the flow reaction described in section 1A was carried out for periods in excess of 8 hr, some 1,2,2-trichloro-1-methyldisilane was obtained. With successive passes through a trap cooled to −36°, it was possible to obtain a mixture that was 70% pure with 1,2-dichloro-1-methyldisilane as the impurity.

F. **Identification of 1,2,2-Trichloro-1-methyldisilane.**—The mass spectrum of a mixture 70% in 1,2,2-trichloro-1-methyldisilane and 30% in 1,2-dichloro-1-methyldisilane (analyzed by an nmr spectrum) contained strong peaks at *m/e* 182, 180, and 178. These peaks were primarily due to the ions $CH_3Si_2H_2{}^{37}Cl_2{}^{35}Cl^+$, $CH_3SiH_2{}^{37}Cl^{35}Cl^{2+}$, and $CH_3Si_2H_2{}^{35}Cl_3^+$. With the ^{30}Si effects, the calculated relative intensities for these ions are 0.39/1.04/1.00 while our experimental relative intensities were 0.37/1.03/1.00. In addition to these peaks, all those expected for this compound and the dichloromethyldisilane were present. No mass spectral peaks for ions heavier than $CSi_2Cl_3H_x^+$ were observed. The proton nmr spectrum of 1,2,2-trichloro-1-methyldisilane consisted of a $-CH_3$ doublet at δ 0.80 (J = 2.2 Hz), a $-HSiCl_2$ doublet at δ 5.73 (J = 3.2 Hz), and a $-HSi(Cl)CH_3$ multiplet at δ 5.01.

G. **Static Reaction of $CH_3Si_2H_5$ with AgCl.**—The static reactions between $CH_3Si_2H_5$ and AgCl were carried out in the reaction vessel described in section 1B. In a typical reaction, 0.93 mmol of $CH_3Si_2H_5$ was condensed into the reaction tube at −196°. The $CH_3Si_2H_5$ was allowed to warm up and remain in contact with the AgCl (heated to 50°) for 1 min. The reactant and volatile products were distilled into the vacuum system and then distilled through a trap cooled to −78°. The fraction that passed this trap was again allowed to react with AgCl. This procedure was repeated 15 times. The final volatile fraction was separated by trap to trap distillations. The condensate in the −196° trap was a mixture of $CH_3Si_2H_5$ and some HCl (0.4 mmol). The condensate in the −78° trap was a mixture of methylchlorodisilanes (0.19 mmol). The nmr spectrum of this mixture indicated that the ratio of $CH_3SiH_2SiH_2Cl$ to $CH_3(Cl)SiHSiH_3$ was 2:1. The condensate in the −45° trap (0.28 mmol) was a mixture of $CH_3(Cl)SiHSiH_2Cl$ and $CH_3(Cl)SiHSiHCl_2$. The products of these reactions were identified as described in sections 2B, D, and F.

3. **$CH_3Si_2H_5$–HCl Reaction over Al_2Cl_6 (Flow).**—The aluminum chloride catalyzed reaction between $CH_3Si_2H_5$ and HCl was carried out in the reaction vessel described for section 1A where Al_2Cl_6 (0.2 g) replaced the AgCl and the traps were cooled to −78°. In a typical experiment, $CH_3Si_2H_5$ (0.60 mmol) and HCl (1.52 mmol) were circulated by the Toepler pump for 8 hr. The products were then separated by trap to trap distillation. Hydrogen (0.13 mmol) was obtained having passed a −196° trap. The condensate in the −95° trap (0.16 mmol) was a mixture of $CH_3(Cl)SiHSiH_3$ and $CH_3SiH_2SiH_2Cl$ in a ratio of 2.5:1. This mixture was identified and analyzed as described in sections 2B and C.

4. **Rearrangement Reactions (Al_2Cl_6 Catalyzed).**—The catalyzed rearrangement reactions of methylchlorodisilanes and 1,2-dichlorodisilane were carried out in a 500-ml long-necked Kjeldahl flask fitted with a Teflon high-vacuum stopcock. Anhydrous Al_2Cl_6 was sublimed into the flask to cover the walls. The Al_2Cl_6 was handled in a drybag prior to the sublimation. The mixtures of chlorinated methyldisilanes or disilanes listed in Table III ((1) 0.27 mmol, (2) 0.72 mmol, (3) 0.33 mmol) were analyzed by an nmr spectrum and a mass spectrum. These mixtures were condensed into the aluminum chloride coated reaction vessel. The product fractions listed in Table III were also analyzed from nmr and mass spectra. The product fraction listed second in Table III was separated by repeated fractionations with −63 and −55° baths. The final fraction condensed at −63° and passing −55° was a 0.54-mmol mixture of 92% $CH_3Cl_2SiSiH_3$ and 8% $CH_3(Cl)SiHSiH_2Cl$. This mixture was identified as follows.

(1) The mass spectrum at 10 V consisted of the following heavy-atom envelopes: $CSi_2Cl_2H_x^+$ (100), $CSi_2ClH_x^+$ (45), and $CSiClH_x^+$ (61). The most intense peak was at *m/e* 144, which was primarily due to the parent ion $CH_3Si_2H_3{}^{35}Cl_2^+$. The calculated intensities at *m/e* 146 and 147 would be 0.72 and 0.15 of the intensity at *m/e* 144 (see section 2D). The experimental intensities at *m/e* 146 and 148 were 0.69 and 0.16 as great as the intensity at *m/e* 144. This mass spectrum eliminated the presence of any methyltrichlorodisilanes or polychlorodisilanes.

(2) The proton nmr spectrum consisted of two singlets at δ 0.99 and 3.51. Very small resonances at δ 4.9, 5.1, and 0.8 indicated the presence of $CH_3(Cl)SiHSiH_2Cl$ (about 8%).

This nmr spectrum demonstrated that $CH_3Si_2H_5$ and both isomers of $CH_3ClSi_2H_4$ and $CH_3SiH_2SiHCl_2$ were not present. The 1,2-$Cl_2Si_2H_4$ was obtained from the reaction of Si_2H_6 and

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[15] E. A. V. Ebsworth and S. G. Frankiss, *Trans. Faraday Soc.*, **63**, 1574 (1967).

[16] H. Vahrenkamp and H. Noth, *J. Organometal. Chem.*, **12**, 281 (1968).

AgCl.[3] Strong absorptions from $ClSi_2H_5$,[3] 1,1,2-$Cl_3Si_2H_3$,[3] Cl_3SiH,[17] or $SiCl_4$[18] were absent from the infrared spectrum of the 1,2-Cl_2SiH_4. However, the infrared spectrum demonstrated that some (about 10%) 1,1-$Cl_2Si_2H_4$[3] was present.

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[17] N. A. Chumavskii, *Opt. Spectrosc. USSR*, **10**, 33 (1961).

[18] D. A. Long, T. V. Spencer, D. N. Waters and L. A. Woodward, *Proc. Roy. Soc.* (*London*), *Ser. A*, **240**, 499 (1957).

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The Acidities of Some Aryl-Substituted Germanes in Liquid Ammonia

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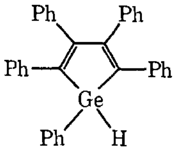
Proton magnetic resonance techniques have been used to determine the acidities of some aryl-substituted germanes in liquid ammonia. It was found that increasing aryl substitution caused a reduction in acidity. Factors such as solvation, ion pairing, and structural effects are used to explain the order of acidities.

Introduction

Although there has been much interest in the acidities of hydrocarbons and the establishment of an acidity scale,[1-3] there is very little information on the analogous hydrides of the other group IV elements. Preliminary work has shown that germane is more acidic than triphenylgermane in liquid ammonia.[4] This is very different behavior from the carbon case where aryl substitution markedly increases acidity by both inductive and resonance effects.[5] The only quantitative study of which we are aware has been carried out by Curtis,[6] who compared the acidity of triphenylgermane with 1,1,3-triphenylpropene in dimethyl sulfoxide. He also showed that pentaphenylgermacyclopentadiene (I) is several orders of magnitude more acidic than triphenylgermane but was unable to obtain an accurate measurement of their relative acidities.



I

We have measured the acidities of some arylgermanes relative to each other and to some hydrocarbon indicators, in liquid ammonia by an nmr method which has already been described.[7] These acidities are discussed in terms of structural and solvation effects upon the acids and their anions.

Experimental Section

Chemicals.—Ammonia was obtained commercially, dried, and stored over sodium metal at −78° until required. Germane, phenylgermane, and di- and triphenylgermanes were prepared and purified as described in the literature.[8-10]

Tri-*p*-tolylgermane (mp 81°, lit.[11] mp 81°) was prepared from *p*-tolylmagnesium bromide by the procedure outlined for triphenylgermane.[11]

Triphenylpropene.—This was prepared by treating phenethylmagnesium bromide with benzophenone to give the alcohol which was subsequently dehydrated with H_2SO_4–CH_3COOH. The product was distilled [210° (0.8 cm)[12]] to yield a mixture of the 1,1,3-triphenylprop-1-ene and 1,3,3-triphenylprop-1-ene isomers. Nmr showed that the 1,1,3 isomer predominated.[13] No attempt was made to separate these isomers since they both yield the same anion upon ionization. Indene was distilled, and fluorene was recrystallized before use.

The purity of all compounds was checked by melting or boiling points and in addition by one or more of nmr, infrared spectroscopy, and mass spectroscopy.

Acidity Measurements.—The method of sample preparation for the acidity measurements has been described previously.[7] For acids and anions of group IV elements, proton exchange is slow on the nmr time scale so that the nmr spectra observed in any one determination consisted of the superimposed spectra of the two acids being compared, their corresponding anions, and the intense ammonia triplet. Fortunately it was possible to choose pairs of acids such that each species present had at least one clearly assignable proton resonance. The relative areas of these absorptions were, in most cases, measured by electronic integration. Occasionally, however, the resonance of interest occurred close to the ammonia triplet preventing electronic integration. In such cases the peak profiles were cut out and the relative areas estimated by accurately weighing the paper profiles. The solutions used were approximately 0.5 *M* in each acid–anion pair.

The nmr samples of lithium, sodium, and potassium germyls were prepared by condensing 2 equiv of germane onto 1 equiv of alkali metal dissolved in ammonia, sealing the nmr tube, and allowing reaction to take place by warming to room temperature. The cesium salt was prepared by treating germane with cesium hydroxide in liquid ammonia. In all cases the excess germane present buffered the solution so that a sharp ammonia triplet was observed. The buffering action controls the [NH_4^+] which has been shown to cause collapse of the ammonia triplet in solutions of water and other acids in liquid ammonia.[14] These solutions were ~0.4 *M* in both GeH_4 and $MGeH_3$.

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[1] A. Streitwieser, Jr., J. H. Hammons, E. Cuiffarin, and J. I. Brauman, *J. Amer. Chem. Soc.*, **89**, 59 (1967).

[2] C. D. Ritchie and R. E. Uschold, *ibid.*, **90**, 2821 (1968).

[3] E. C. Steiner and J. D. Starkey, *ibid.*, **89**, 2751 (1967).

[4] T. Birchall and W. L. Jolly, *Inorg. Chem.*, **5**, 2177 (1966).

[5] A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965).

[6] M. D. Curtis, *J. Amer. Chem. Soc.*, **91**, 6011 (1969).

[7] T. Birchall and W. L. Jolly, *ibid.*, **88**, 5439 (1966).

[8] W. L. Jolly and J. E. Drake, *Inorg. Syn.*, **7**, 34 (1963).

[9] K. Kuehlen and W. P. Neumann, *Ann.*, **702**, 17 (1967).

[10] O. H. Johnson, *Inorg. Syn.*, **5**, 74 (1961).

[11] F. Glocking and K. Hooton, *J. Chem. Soc.*, 3509 (1962).

[12] C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, **6**, 534 (1941).

[13] N. Campbell and K. W. Delahunt, *J. Chem. Soc. C*, 1810 (1966).

[14] T. Birchall and W. L. Jolly, *J. Amer. Chem. Soc.*, **87**, 3007 (1965).