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NMR SPECTRA OF HALOPERMETHYLPOLYSILANES

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Summary

Proton NMR spectra were determined for the series $X(SiMe_2)_nX$ (n = 3, 4, 6 and X = F, Cl, I) and $Me(SiMe_2)_6X$. Fluorine-19 NMR spectra for the fluorosilanes of these series were also determined. The chemical shift of the methyl protons of the $SiMe_2X$ group appears at higher field as the chain length increases. This chemical shift also is at higher field for monohalopolysilanes than for the corresponding dihalopolysilanes. These observations are consistent with increased donation from halogens to vacant polysilane orbitals with increased chain length and with transmission of the effect of a second halogen through the silicon chain.

Introduction

In a recent report of the reactions of α,ω-dichloropermethylpolysilanes with methylmagnesium iodide it was suggested that increased donation of electrons from chlorine into vacant polysilane orbitals occurs with increasing chain length [1]. In addition to this, the effect of the second chlorine appears to be transmitted through the silicon chain resulting in a greater reactivity of the α,ω-dichloropermethylpolysilane toward the Grignard reagent than of the 1-chloropermethylpolysilane of the same chain length. Furthermore, the proton resonance in methyl protons of the $SiMe_2Cl$ group was observed in all cases to occur at a higher field for $Me(SiMe_2)_nCl$ than for the corresponding $Cl(SiMe_2)_n$-Cl. To obtain additional information, we undertook an extensive study of the NMR chemical shifts of related compounds.

Only one systematic study of chemical shifts in linear permethylpolysilanes has been reported [2]. The effect of substituents on the proton NMR properties of methylated disilanes and trisilanes was examined along with the determination of chemical shifts for members of the permethylpolysilane series.

Results and discussion

Proton NMR chemical shifts are given in Table 1 for several permethyl-, fluoropermethyl-, chloropermethyl-, and iodopermethyl-polysilanes. Also included in this table are the shifts for the compounds $ClMe_2Si(CH_2)_4SiMe_2Cl$, $Me_3Si(CH_2)_4SiMe_2Cl$, and $Me_3Si(CH_2)_4SiMe_3$. In Table 2, ^{19}F chemical shifts an coupling constants, J(HF), are given for the fluoropermethylpolysilanes.

Trends of chemical shifts

From the data in Tables 1 and 2, the following trends are apparent:

(1) With increasing chain length, the proton resonance of the $SiMe_2X$ methyl groups tends to shift upfield in the $X(SiMe_2)_nX$ series.

(2) The chemical shifts of the $SiMe_2X$ methyl protons for the monohalopermethylhexasilanes occur upfield from those of the corresponding dihalopermethylhexasilanes. This trend has also been seen for other chain lengths in the chloropermethylpolysilane series [1].

(3) With increasing chain length, the ^{19}F resonance tends to move downfield in the $F(SiMe_2)_nF$ series.

(4) In the monohalopermethylhexasilanes, a small downfield shift of the terminal $SiMe_3$ group with respect to the permethylhexasilane is seen. No significant variation in this shift as a function of halogen is seen.

TABLE 1

PROTON NMR CHEMICAL SHIFTS[a]

Compound	$SiMe_2X$	$SiMe_2$	$SiMe_3$
$Me(SiMe_2)_2Me$	—	—	0.040
$Me(SiMe_2)_3Me$	—	0.075	0.085
$Me(SiMe_2)_4Me$	—	0.112	0.093
$Me(SiMe_2)_6Me$	—	0.130, 0.180	0.093
$F(SiMe_2)_3F$[c]	0.361[b]	0.191	—
$F(SiMe_2)_4F$[c]	0.340[b]	0.181	—
$F(SiMe_2)_6F$[c]	0.320[b]	0.193, 0.178	—
$Me(SiMe_2)_6F$[d]	0.290[b]	0.199, 0.170, 0.145	0.098
$Cl(SiMe_2)_3Cl$	0.530	0.262	—
$Cl(SiMe_2)_4Cl$	0.515	0.258	—
$Cl(SiMe_2)_6Cl$	0.500	0.233, 0.247	—
$Me(SiMe_2)_6Cl$	0.463	0.145, 0.198, 0.262, 0.282	0.100
$I(SiMe_2)_3I$[e]	0.940	0.284	—
$I(SiMe_2)_4I$[e]	0.933	0.249	—
$I(SiMe_2)_6I$[e]	0.893	0.288, 0.247	—
$Me(SiMe_2)_6I$[f]	0.863	0.148, 0.216, 0.231	0.098
$Me_3Si(CH_2)_4SiMe_3$	—	—	0.025
$Me_3Si(CH_2)_4SiMe_2Cl$	0.390	—	0.025
$ClMe_2Si(CH_2)_4SiMe_2Cl$	0.390	—	—

[a] All shifts are for 2—5% cyclohexane solutions at 35° and are expressed in ppm downfield from TMS. All spectra were obtained on either a Varian Associates Model T-60 or a Perkin—Elmer Hitachi Model R-20B spectrometer. [b] Center of doublet. [c] Prepared by reaction of the corresponding iodopermethylpolysilane with AgF [3]. [d] Prepared by reaction of $Me(SiMe_2)_6Cl$ with HF in 50% methanol [4]. [e] Prepared by Stolberg's method [5]. [f] Prepared by stirring $Me(SiMe_2)_6Cl$ with MgI_2.

TABLE 2

^{19}F CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS

Compound	Shift	J(H—F) (Hz)
$F(SiMe_2)_3F$	101.15[b]	8.6 ± 0.2
$F(SiMe_2)_4F$	96.70[b]	8.4
$F(SiMe_2)_6F$	95.25[b]	8.3
$Me(SiMe_2)_6F$	96.80[b]	8.2

[a] All shifts are for 2—5% solutions at 35° in cyclohexane and are expressed in ppm upfield from 1% CF_3COOH in chloroform (external reference). [b] Center of septet.

Trends (1) and (3) are consistent with earlier observations [6] that interactions between Lewis bases and silanes become more favorable with increasing chain length.

Lack of association

Several studies were carried out to evaluate the role of either inter- or intra-molecular associations in causing the observed trends in shifts.

Variable temperature NMR studies (90 MHz) of 1,6-dichloropermethylhexasilane and trimethylchlorosilane show changes in chemical shifts of only ~ 3.5 Hz for each compound in going from + 25 to — 100°C. The shift due to concentration is only ~ 0.5 Hz between 2 and 20%. This concentration is consistent with West's observations [2].

In the fluorine-19 NMR spectra of fluoropermethylpolysilanes, septets arise from the splitting by the six methyl protons of the $SiMe_2F$ group. In the proton NMR spectra of these compounds, the $SiMe_2F$ protons exhibit a doublet. A species associated by halogen-bridging should give more extensive splitting. A halogen-bridged species with rapidly exchanging halogens should result in a collapse of the observed splittings.

The chemical shifts of the $SiMe_3$ and $SiMe_2X$ groups in the series $Me_3Si(CH_2)_4SiMe_3$, $Me_3Si(CH_2)_4SiMe_2Cl$, $ClMe_2Si(CH_2)_4SiMe_2Cl$ remain constant. Therefore, the origin of the difference between shifts of the $SiMe_2X$ methyl protons of the mono- and di-halopermethylpolysilanes apparently depends upon the silicon chain.

Solvent effects

A solvent effect on the chemical shifts of the chloropermethylpolysilanes

TABLE 3

SOLVENT EFFECTS ON SHIFTS

Compound	Solvent	$SiMe_2Cl$	$SiMe_2$	$SiMe_3$
1,4-Dichlorooctamethyltetrasilane	CCl_4	0.511	0.255	—
	C_6H_{12}	0.515	0.258	—
	$(C_2H_5)_2O$	0.498	0.245	—
Permethyltetrasilane	CCl_4	—	0.113	0.093
	C_6H_{12}	—	0.112	0.093
	$(C_2H_5)_2O$	—	0.109	0.077

can be seen by comparing the chemical shifts given in Table 1 with those previously reported in ethyl ether solution [1]. The shifts in ethyl ether are from 0.010 to 0.030 ppm upfield from those in cyclohexane at comparable concentrations. No significant solvent effect was noticed between carbon tetrachloride and cyclohexane (see Table 3).

Conclusion

On the basis of the variable temperature studies, the fluoropermethylpolysilane spectra and the chemical shifts of the methylene analogs, inter- and intramolecular associations can be ruled out as being responsible for the trends observed. The observed trends in chemical shifts can best be explained by increased donation of electron density into vacant polysilane orbitals with increasing chain length and by the transmission of the effect of halogens through the silicon chain.

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