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The Preparation, Properties and Isomeric Form of Methyl Pseudohalogeno Silanes

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Abstract

Methyl pseudohalogeno silanes CH_3SiH_2X (X = CN, NCO, NCS, or NCSe), were prepared by the interaction of CH_3SiH_2Br with the appropriate dry silver pseudohalide, characterized, and the isomeric form determined by infrared spectroscopy. Methylsilyl cyanide possesses the normal structure with a Si–C linkage, while other pseudohalides possess an iso structure with a Si–N linkage.

Introduction

Preparation and physical properties of several alkylsilanes, R_nSiH_{4-n} ($R = CH_3, C_2H_5$; n = 1–4), were described earlier [1, 2]. Later, syntheses of some monomethyl silyl derivatives, $(CH_3SiH_2)_n$ X, ($X = CH_3$, F, Cl, Br, I, or NC when n = 1; X = O or S when n = 2; X = N when n = 3) and their characterizations were also reported [3, 4]. One of these compounds, methylsilyl(iso)cyanide, which was obtained from the interaction of CH_3SiH_2I and AgCN, was considered an interesting case of structural isomerism. Although various other organosilyl and silyl pseudohalides have since been prepared and their properties and structures investigated [5–7], the above cyanide has been the only CH_3SiH_2 pseudohalide investigated thus far [3]. With a view of investigating whether pseudohalogens other than cyanide in compounds having both CH_3Si and SiH_2 linkages also display any structural isomerism, the methylsilyl-(iso)thiocyanate, -(iso)selenocyanate, -(iso)cyanate, as well as the cyanide, were prepared and characterized, and their structures were determined.

Experimental

All volatile methylsilyl compounds were handled and their reactions were carried out in a high vacuum system [8]. The standard taper joints and stopcocks of the pyrex high vacuum apparatus were lubricated with Apiezon-N grease.

Preparation of Starting Materials

Methylsilane (CH_3SiH_3) was prepared by the reduction of CH_3SiCl_3 with $LiAlH_4$(2) and methylbromosilane (CH_3SiH_2Br) was obtained by the bromination of CH_3SiH_3 with HBr in the presence of an Al_2Br_6 catalyst at room temperature. The purity of CH_3SiH_3 and of CH_3SiH_2Br was checked by molecular weight measurement.

Preparation of Methylsilyl Pseudohalides

A measured amount of CH_3SiH_2Br, which was pre-condensed in a trap, was allowed to pass through a column packed with freshly prepared silver pseudohalide (CN, NCS, NCSe, NCO) for about 30 min at room temperature. An exothermic reaction resulted with formation of yellow AgBr. The reaction products were condensed into an adjacent trap and cooled to −196° with liquid nitrogen. Methylsilyl pseudohalide was separated from unreacted CH_3SiH_2Br, if any, and purified by low temperature trap-to-trap distillation.

The melting points of the purified methylsilyl pseudohalides were determined by Stock's magnetic plunger apparatus, and their molecular weights were determined by the direct weight method [8]. The vapor pressures of the compounds at different temperatures were measured using a mercury manometer. The temperatures were measured with calibrated copper-constantan thermocouples in conjunction with a sensitive potentiometer. The analysis of the compounds for C, H, and N was carried out in the vapor phase using standard analytical techniques. The infrared spectra were examined in the vapor phase in both the 4000–650 and 650–300 cm^{-1} regions on a Perkin Elmer Spectrophotometer model 521 in specially designed gas cells (10 cm length and 5 cm diameter) which were fitted with NaCl or CsBr windows.

Results and Discussion

The melting point, molecular weight, yield, elemental analysis, and vapor pressure at 0 °C (calculated from the vapor pressure curve representing a plot of $\log_{10} P$ (mm) against 1/t × 10^4 of four methylsilyl pseudohalides is shown in Table I. The vapor pressures of the compounds at different temperatures are given in Table II. The values are reversible; increasing or decreasing the temperature gave reproducible results and thus indicates no decomposition occurred during the determination.

Infrared Spectra

Infrared active absorptions associated with pseudohalides and Si-pseudohalide groups in the newly prepared compounds are shown in Table III; those due to CH_3, SiH_2 and Si–CH_3 are listed in Table IV.

CH_3, SiH_2 and Si–CH_3 Absorptions

The absorptions due to CH_3, SiH_2 and Si–CH_3 have been assigned on the basis of the reported spectra of CH_3SiH_2– and CH_3CH_2–derivatives [3, 4, 9].

Two of the three bands observed in the region 3000–2900 cm^{-1} have been assigned to the CH_3 asymmetric stretching vibration and the remaining one to its symmetric mode. The main strong absorption and a shoulder at 2200–2190 cm^{-1} are due to two Si–H stretching vibrations. The weak broad band at 1450–1425 cm^{-1} and a doublet at 1273–1258 cm^{-1} may be assigned to the asymmetric and symmetric deformation of the CH_3 group, respectively. The strong absorptions at 960 and 910 cm^{-1} observed in the spectra of four methylsilyl pseudohalides do not have any counterpart in fully methylated derivatives of silane [10] and methyl chlorosilanes [11] and therefore must be associated with the SiH_2 group. The former is attributed to SiH_2 scissoring and the latter to the corresponding wagging mode. The absorptions at 880–870 and ~760 cm^{-1} are due to CH_3 rocking and Si–CH_3 stretching modes, respectively [4]. The twisting and rocking modes of the SiH_2 group occur at 712–707 and 510–505 cm^{-1}, respectively. These vibrations are independent of the electronegativity of the substituent atom [4]. The Si–CH_3 torsion could not be located in the spectrum of any of the compounds and is expected to be a very weak band at low frequencies.

TABLE I. Analytical Data for Methylsilyl Pseudohalides.

	Yield (%)	M.P. (°C)	V.P. at 0 °C (mm)	Mol. Wt. Found (Calcd)	Elemental analysis (%) Found (Calcd.)		
					C	H	H
CH_3SiH_2CN	80	−25.4, −25.2[a]	26.3	71.1, 71.2 (71.1)	34.11 (33.76)	6.27 (7.08)	19.16 (19.69)
CH_3SiH_2NCS	86	−81.4, −81.6	5.5	104.1 (103.2)	23.50 (23.27)	4.70 (4.88)	13.37 (13.57)
CH_3SiH_2NCSe	83	−73.6, −73.2	2.9	149.0 (150.1)	16.07 (16.00)	3.27 (3.36)	(9.10) (9.33)
CH_3SiH_2NCO	75	−90.5, −91.2	75.8	87.1, 88.1 (87.1)	27.40 (27.56)	5.70 (5.78)	(16.10) (16.07)

[a] Reported −23.1 °C.

TABLE. II. Vapor Pressure of Methylsilyl Pseudohalides.

H_3CSiH_2CN		H_3CSiH_2NCO		H_3CSiH_2NCS		H_3CSiH_2NCSe	
Temp. (°C)	V.P. (mm)	Temp. (°C)	V.P. (mm)	Temp. (°C)	V.P. (mm)	Temp. (°C)	V.P. (mm)
−40.0	1.7	−52.7	3.0	−18.6	1.2	−19.2	1.5
−31.8	3.4	−46.4	4.7	−14.6	2.0	−8.8	2.1
−24.2	6.0	−31.4	14.6	−4.2	4.2	0	2.8
−16.8	9.6	−25.2	22.2	0.4	5.5	9.2	3.7
−7.2	17.2	−12.8	46.5	3.6	6.6	15.2	4.7
0.2	26.0	0	89.4	8.0	9.5		
6.0	34.8	6.2	115.0	11.0	10.3		
17.8	63.8	12.2	136.5	15.0	13.0		

TABLE III. Infrared Frequencies (cm^{-1}) associated with Pseudohalide and Si-Pseudohalide Groups in Methyl Silyl Pseudohalides.

CH_3SiH_2CN	CH_3SiH_2NCO	CH_3SiH_2NCS	CH_3SiH_2NCSe	Assignment
	2310vs			$\nu_{asymm.}$ –N=C=O
2203s[a]				$\nu_{C\equiv N}$
		2088–2035vs (br)		$\nu_{asymm.}$ –N=C=S
			2047s	$\nu_{asymm.}$ –N=C=Se
	1450s			$\nu_{symm.}$ –N=C=O
		1026m		$\nu_{symm.}$ –N=C=S
	616m (br)			δ–N=C=O
589m				νSi–C≡N
	570m			νSi–N=C=S
		492w		δ–N=C=S
466w				δSi–CN (Overtone)
		449w		νSi–N=C=S
	310			δSi–N=C=O

[a] v = very; s = strong; m = medium; w = weak; br = broad.

TABLE IV. IR Absorptions (cm^{-1}) of CH_3, SiH_2, and Si–CH_3 Groups.

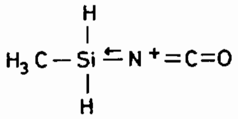
Region (cm^{-1})	CH_3SiH_2CN	CH_3SiH_2NCO	CH_3SiH_2NCS	CH_3SiH_2NCSe	Assignment
3000–2900	2 Absorptions	2 Absorptions	1 Absorption	1 Absorption	$\nu_{asymm.}$ CH_3
	1 Absorption	1 Absorption	1 Absorption	1 Absorption	$\nu_{symm.}$ CH_3
2200–2190	Masked by	1 Absorption	1 Absorption	1 Absorption	νSiH_2
	νC≡N	1 Absorption (Sh)	1 Absorption (Sh)	1 Absorption	νSiH_2
1450–1425	1 Absorption (w, br)	Masked by νSymm. N=C=O	Absent	1 Absorption (w, br)	$\delta_{asymm.}$ CH_3
1273–1258	Doublet	Doublet	Doublet	Doublet	$\delta_{symm.}$ CH_3
~960	1 Absorption	1 Absorption	1 Absorption	1 Absorption	Si–H_2 Scissors (δ)
~910	1 Absorption	1 Absorption	1 Absorption	1 Absorption	Si–H_2 Wagging (δ)
880–870	1 Absorption	1 Absorption	1 Absorption	1 Absorption	CH_3 Rock
~760	1 Absorption	1 Absorption	1 Absorption	1 Absorption	νSi–CH_3
712–707	1 Absorption	1 Absorption	1 Absorption	1 Absorption	Si–H_2 Twisting
510–505	1 Absorption	1 Absorption	1 Absorption	1 Absorption	Si–H_2 Rocking

Pseudohalide and Si–pseudohalide Absorptions

The strong absorption at 2203 cm^{-1} in the spectrum of methylsilyl cyanide may be attributed to the C≡N stretching vibration [12, 13]. Extensive studies on organosilicon cyanides have shown that the strong absorption at ~2200 cm^{-1} represents the normal cyanide isomer and a weaker band at ~2100 cm^{-1} represents an isocyanide form [13, 14]. Organic isocyanides also give C≡N absorptions at lower frequencies than the nitriles [15]. Also, the 2100 cm^{-1} band due to isocyanide has been doubted by Ebsworth [14], who believed it to be due to an overtone or combination mode strengthened by the Fermi resonance with a C≡N stretching fundamental. Thus, identification of a Si–C≡N stretching vibration at 589 cm^{-1} in addition to a Si–CH_3 mode supports the normal structure for the compound [12]. The Si–C≡N deformation mode probably falls below the recorded range. However, a weak band at 466 cm^{-1} may be an overtone of the Si–C≡N deformation, which would place the fundamental around 233 cm^{-1} [12].

The absorptions at 2300–2250 cm^{-1} and 1460–1435 cm^{-1} in the spectra of silyl isocyanates [16] and methylsilyl di- and triisocyanates [17, 18] have been assigned to –N=C=O asymmetric and symmetric stretching vibrations, respectively. However, organic normal cyanates and isocyanates both show asymmetric stretching in the same region, 2300–2200 cm^{-1}, but differ in the symmetric vibration, which occurs at 1450–1400 cm^{-1} in organic isocyanates [19] and below 1200 cm^{-1} in normal cyanates [20]. Accordingly, the bands at 2310 cm^{-1} and 1450 cm^{-1} observed in the spectrum of methylsilyl (iso)cyanate have been attributed to the asymmetric and symmetric stretching of the –N=C=O group and hence the iso arrangement with a Si–N linkage [16, 17]. Only one –N=

C=O deformation at 616 cm^{-1} could be identified in the spectrum of this compound [17, 18]. The asymmetric and symmetric stretching and deformation vibrations of –N=C=O group occur at slightly higher frequencies in the spectrum of monomethyl silyl (iso)cyanate than those in the spectrum of its carbon analog [19], contrary to what would be expected from the mass effect. $(p \rightarrow d)_\pi$ bonding between nitrogen and silicon atom [21, 22], which gives partial double bond character to the Si–N linkage, would counteract the mass effect.



$$H_3C-\overset{\displaystyle H}{\underset{\displaystyle H}{Si}}\leftharpoondown N^{+}=C=O$$

The absorption at 570 cm^{-1} appears to be associated with the Si–N=C=O stretching vibration, which is slightly higher (~525 cm^{-1}) than in other organosilyl (iso)cyanates [17, 18]. The deformation mode of the Si–N=C=O group could tentatively be assigned to the weak band at 310 cm^{-1} [18].

A very strong and broad band at 2088–2035 cm^{-1} and a medium band at 1026 cm^{-1} in the spectrum of methylsilyl (iso)thiocyanate can be attributed to the asymmetric and symmetric stretching of the –N=C=S group, respectively. The asymmetric –N=C=S stretching vibration appears as single, double, or even triple bands in the region 2100–2000 cm^{-1}, and the symmetric vibration at 1050–956 cm^{-1} in the spectra of various silyl and methylsilyl isothiocyanates and the presence of the Si–N linkage was established and confirms an iso structure for the (iso)thiocyanate derivatives [21, 23]. Also, the position of the symmetric –N=C=S stretching vibration has been very reliable in distinguishing between normal and iso structures of the organic thiocyanates [24]. This absorption occurs between 1100–950 cm^{-1} in the spectra of organic isothiocyanates and ~700 cm^{-1} in organic thiocyanates [25, 26]. The intensity and shape [27] of the –N=C=S asymmetric stretching band further support an iso structure for methylsilyl (iso)thiocyanate. A band at 492 cm^{-1}, which is attributable to –N=C=S deformation, and another at 449 cm^{-1}, a Si–N=C=S stretching vibration, could also be located with certainty [18, 21]. However, Si–N=C=S deformation could not be observed; it is expected to be very weak and below 300 cm^{-1} [18].

Selenocyanates, like thiocyanates, also exhibit isomerism. Organometallic selenocyanates show a sharp band of moderate intensity at 2140–2100 cm^{-1} and a weak band at 590–530 cm^{-1}, asymmetric and symmetric stretching of –Se–C≡N, respectively [28, 29]. However, organometallic isoselenocyanates, including organosilyl and silyl derivatives, give a strong broad absorption at 2108–2050 cm^{-1} and a weaker absorption at 625–600 cm^{-1} due to the two stretching vibrations [29, 30]. Accordingly, the strong broad band at 2047 cm^{-1} and the weaker one at 617 cm^{-1} that are observed in the spectrum of methylsilyl (iso)selenocyanate have been assigned to the asymmetric and symmetric stretching of –N=C=Se and the pseudohalogen group appears to be bonded to Si through N [30]. The absorptions associated with –N=C=Se deformation or Si–N=C=Se stretching and deformation could not be located.

Nuclear Magnetic Resonance

Chemical shift and coupling constant data for CH_3SiH_2Ps and $CH_3SiH(NCO)_2$ compounds are given in Table V.

TABLE V. Chemical Shift[a] and Coupling Constant Data for CH_3SiH_2Ps and $CH_3SiH(NCO)_2$.

	δ Si–H (ppm)	Si–H dilution shift (Hz)	δCH (ppm)	CH_3 dilution shift (Hz)	$J_{H-H'}$ (cps)	$J^{29}SiH$ (Hz)	$J^{13}CH$ (Hz)	Internal chem. shift (ppm)
H_3SiCN	3.82							
CH_3SiH_2CN	−3.99	0.7	+0.40	2.0	4.27	228.5	125.0	4.39
H_3SiNCO	4.42							
CH_3SiH_2NCO	−4.48	0	+0.30	2.6	3.6	224.5	119.0	4.78
H_3SiNCS	4.46							
CH_3SiH_2NCS	−4.56	10.2	+0.43	8.3	3.7			4.99
$H_3SiNCSe$	4.48							
CH_3SiH_2NCSe	−4.56	8.0	+0.41	10.7	3.7	233.0	121.0	4.97
$CH_3SiH(NCO)_2$	−4.79	2.4	+0.38	1.6	2.5	265.0	120.0	5.17
CH_3SiH_3	−2.11		+1.32					
CH_3SiH_2Br	−3.05		+0.76					

[a] A negative sign indicates a downfield shift and a positive sign indicates an upfield shift from cyclohexane.

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