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Study of Some Mixed Silyl Germyl Group VIa Derivatives

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The synthesis of GeH_3SSiH_3 and $GeH_3SSi(CH_3)_3$ has been achieved by the interaction of a 1:1 mole ratio of GeH_3Cl with $(SiH_3)_2S$ and GeH_3F with $[(CH_3)_3Si]_2S$, respectively. Germyl trimethylsilyl ether, $GeH_3OSi(CH_3)_3$, has been prepared by the interaction of $(CH_3)_3SiOLi$ with GeH_3Cl. The complete characterization of the mixed silyl germyl group VIa derivatives has not been possible owing to the tendency for the compounds to readily undergo disproportionation in the liquid phase. Infrared and ^1H nuclear magnetic resonance spectral data for the compounds are presented.

Introduction

Many of the important conclusions about the bonding characteristics of silicon and germanium have been obtained from studies of various hydride derivatives of these elements rather than from analogous organosilicon and organogermanium compounds.[1–3] Selecting the hydrides for study is especially important in cases where the organic substituents may influence the results in a significant way. Thus, in order to obtain information about the nature of the heteroatom Si–O–Ge and Si–S–Ge linkages, it would be most desirable to be able to work with the simple silyl, (SiH_3), and germyl, (GeH_3), derivatives. In this report, we present the results of research carried out to ascertain whether or not compounds of this general type could be prepared and studied.

Experimental Section

Apparatus. With the exception of the synthesis of some of the starting materials, all work was carried out in a conventional Pyrex-glass vacuum system.[4] Apparatus and techniques employed were identical with those previously described.[5]

Materials. Germyl chloride (vapor pressure at 0°: found, 236 Torr; lit.,[6] 234 Torr; purity confirmed by its infrared spectrum[7]) and GeH_3Br (mol wt: found, 155.7; calcd, 155.5; purity confirmed by its infrared spectrum[7]) were prepared by the reaction of GeH_4 with $SOCl_2$[8] and Br_2,[9] respectively. Germyl fluoride (purity confirmed by its infrared spectrum[7]) was prepared by passing GeH_3Br through a column of freshly prepared PbF_2.[10] Disilyl sulfide (vapor pressure at 0°: found, 61 Torr; lit.,[11] 61 Torr; purity confirmed by its infrared spectrum[12]) and $[(CH_3)_3Si]_2S$ (purity checked by its infrared spectrum[13]) were prepared by passing the vapors of SiH_3I and $(CH_3)_3SiI$, respectively, through a column packed with red HgS and dry sand.[11] Lithium trimethylsilanolate was prepared by reaction of CH_3Li with $[(CH_3)_3Si]_2O$.[14]

Synthesis and Identification of GeH_3SSiH_3. Germyl chloride (0.8 mmol) and $(SiH_3)_2S$ (0.8 mmol) were condensed into a 50-ml reaction vessel and allowed to stand for 5 min at room temperature. The products were distilled through traps maintained at −46, −96, and −196°. The trap at −196° contained SiH_3Cl (0.8 mmol, identification made by its infrared spectrum[15]). The trap at −46° contained a small amount of $(GeH_3)_2S$ (identification made by its infrared spectrum[16]). The infrared spectrum of the contents of the −96° trap was consistent with that expected for the mixed sulfide GeH_3SSiH_3, although the spectrum revealed the presence of a small amount of $(SiH_3)_2S$ by its characteristic Si–S symmetric stretching mode at 479 cm^{-1}. Attempts to remove the impurity were not successful and, in fact, the concentration of impurity increased after several additional purification attempts. Further studies (see below) indicated that the compound easily underwent disproportionation to form $(SiH_3)_2S$ and $(GeH_3)_2S$. Digermyl sulfide could easily be removed from the product mixture by standard fractionations, but because of their similar volatilities, $(SiH_3)_2S$ could not be removed from the GeH_3SSiH_3. The use of gas chromatography also failed to purify the mixed sulfide, even with the identical column and conditions used previously to purify GeH_3SCH_3.[17]

The formation of GeH_3SSiH_3 in the reaction was unequivocally established by the compound's characteristic proton nmr spectrum. The spectrum of a 14% by volume sample in deuteriocyclohexane (TMS added as an internal standard) consisted of two 1:3:3:1 quartets (J_{HH} = 0.8 Hz) of equal intensity centered at τ 5.59 (±0.01) (SiH_3 protons) and τ 5.41 (±0.01) (GeH_3 protons). The data are in agreement with the values obtained for this compound (prepared by an alternate route) by other workers.[18]

Synthesis of $(GeH_3)_2S$. Since it was noted in our laboratory that the purification steps in the commonly quoted synthesis of $(GeH_3)_2S$ (based on the reaction of GeH_3I with HgS) are often very tedious, we carried out a small-scale "clean" synthesis of the compound based on the reaction of pure $(SiH_3)_2S$ (1 mmol) with pure GeH_3Cl (2 mmol). The reactants were condensed into a 50-ml tube and allowed to react for 5 min. Pure $(GeH_3)_2S$ (1.0 mmol) was isolated from the products in a −45° trap in one standard vacuum-line distillation from room temperature to −45° to −196°. The purity of the material was confirmed by its infrared spectrum[16] and by its vapor pressure at 0° (5.0 Torr, lit.[16] value 5.0 Torr).

Synthesis and Identification of $GeH_3SSi(CH_3)_3$. Germyl fluoride (0.8 mmol) and $[(CH_3)_3Si]_2S$ (0.8 mmol) were condensed into a 50-ml reaction vessel and allowed to stand for 5 min at room temperature. The products were distilled through traps maintained at −83 and −196°. An infrared analysis of the two fractions indicated that the trap at −196° contained mostly $(CH_3)_3SiF$[19] with some GeH_3F[7] and a trace of GeH_4,[20] while the trap at −83° contained $[(CH_3)_3Si]_2S$,[13] $(GeH_3)_2S$,[16] and the mixed sulfide $GeH_3SSi(CH_3)_3$. Absorptions in the nmr spectrum of the sample (14% by volume in deuteriocyclohexane with C_6H_{12} added as an internal standard) confirmed the presence of $[(CH_3)_3Si]_2S$ (τ 9.67) and $(GeH_3)_2S$ (τ 5.38).[17,21]

The two remaining singlets present in a 3:1 ratio at τ 9.69 and 5.57 are assigned to the CH_3 and GeH_3 protons, respectively, in $GeH_3SSi(CH_3)_3$. It was not possible to purify the sample further by using standard trap to trap distillations. A portion of the material was distilled by using a low-pressure fractionating column similar to the one described by Jolly.[22] All of the $[(CH_3)_3Si]_2S$ and most of the $(GeH_3)_2S$ could be removed from the $GeH_3SSi(CH_3)_3$ by using this column. Further attempts to remove the small amount of $(GeH_3)_2S$ from the sample resulted in the formation of both $[(CH_3)_3Si]_2S$ and $(GeH_3)_2S$.

Synthesis and Identification of $GeH_3OSi(CH_3)_3$. This compound was prepared by the reaction of $(CH_3)_3SiOLi$ with GeH_3Cl. Several variations in the experimental method were tried and the following details represent what we found to be the optimum conditions for the synthesis.

The inside of a 500-ml round-bottom flask was coated with a tetrahydrofuran (THF) solution containing about 2 mmol of $(CH_3)_3SiOLi$.[14] The flask was attached to the vacuum line and evacuated for 48 hr until no pressure buildup from THF could be detected. The $(CH_3)_3SiOLi$ was very light brown and flaky. After condensing 2 mmol of GeH_3Cl into the flask, the reactants were allowed to warm slowly to room temperature. During this slow warm-up period, the reaction vessel was opened to a series of traps maintained at −78 and −196°. The product condensed in the trap at −78° while unreacted GeH_3Cl passed on to the trap at −196° and was later recondensed into the reaction vessel for further reaction. After five cycles of recondensing the unreacted GeH_3Cl into the vessel, only a trace of material passed through the −78° trap.

The nmr spectrum of the contents (17% by volume in deuteriocyclohexane with C_6H_{12} added as an internal standard) of the −78° trap indicated that $GeH_3OSi(CH_3)_3$ was the major product of the reaction, although a small amount of $[(CH_3)_3Si]_2O$ (shoulder at τ 9.93[21]) and a trace amount of THF (complex peaks centered at about τ 6.25 and 8.15, lit.[23] values τ 6.25 and 8.15) were present in the sample. The major absorptions in the spectrum were found at τ 9.95 and 4.82 in a 3:1 ratio and readily assigned to the CH_3 and GeH_3 resonances of the mixed ether. For identification purposes, it should be noted that although the CH_3 protons of the mixed ether and $[(CH_3)_3Si]_2O$ have similar resonance frequencies, the GeH_3 resonance of $GeH_3OSi(CH_3)_3$ is distinctly shifted from that of $(GeH_3)_2O$ (τ 4.73).[24]

Attempts to purify the compound further resulted in the formation of additional $[(CH_3)_3Si]_2O$ and $(GeH_3)_2O$, as determined by infrared and nmr analyses. It was not possible to separate the three components of resulting fractions.

Mass Spectrum. The mass spectrum of germyl trimethylsilyl ether is complex due to the existence of five isotopes of germanium in significant natural abundance coupled with the tendency of the compound to decompose. The molecular weights of $GeH_3OSi(CH_3)_3$ and its disproportionation products $[(CH_3)_3Si]_2O$ and $(GeH_3)_2O$ are comparable (164.8, 162.4, and 167.2, respectively) so that some *m/e* values can be attributed to fragments of all three compounds. The fragmentation pattern is not reported as the mass spectrum does not represent pure $GeH_3OSi(CH_3)_3$.

The precise mass of the fragment corresponding to $^{70}GeC_2SiH_9O^+$ (parent mixed ether minus CH_3) was determined to be 146.9660 (calculated value 146.9665).

Stability Studies of $GeH_3OSi(CH_3)_3$, $GeH_3SSi(CH_3)_3$, and GeH_3SSiH_3. A vapor-phase sample of each compound was expanded into a glass infrared cell fitted with KBr windows and allowed to stand at room temperature for several hours. Spectra were recorded initially and then hourly. In all three cases, the initial and subsequent spectra were identical. The samples, pressures, and test times were as follows: $(CH_3)_3SiOGeH_3$, 11.0 Torr, 3 hr; SiH_3SGeH_3, 15.0 Torr, 7.5 hr; $(CH_3)_3SiSGeH_3$, 6.9 Torr, 6.5 hr.

Neat liquid samples of each compound were allowed to stand at room temperature in glass tubes. Noncondensables were removed and the remaining volatile materials were identified by infrared analyses. After 3 days, the $GeH_3OSi(CH_3)_3$ sample decomposed to form a brownish solid, noncondensable material, and some condensable products identified as being a mixture of GeH_4[20] and $[(CH_3)_3Si]_2O$.[13] After 3 days, GeH_3SSiH_3 decomposed to form a brown solid, noncondensables, and condensable material identified as being $(SiH_3)_2S$,[12] GeH_3SSiH_3, $(GeH_3)_2S$,[16] and GeH_4.[20] After 5 days, $(SiH_3)_2S$, GeH_4, and a trace of SiH_4[25] were identified in the products of the decomposition. After several hours, $GeH_3SSi(CH_3)_3$ partially decomposed to form $(GeH_3)_2S$ and $[(CH_3)_3Si]_2S$. After 5 days, approximately half of the sample decomposed, the sole products being equivalent amounts of $(GeH_3)_2S$ and $[(CH_3)_3Si]_2S$.

Similar trends were noted when samples of the compounds were placed in solution and the decomposition reactions were monitored by nmr methods. In the decomposition of $GeH_3OSi(CH_3)_3$ (17% by volume in cyclohexane), the $GeH_3OSi(CH_3)_3$ absorptions steadily decreased over a period of several hours. A $(GeH_3)_2O$ absorption at τ 4.73[24] appeared after 6 hr and remained relatively weak until it disappeared after 18.5 days. The $[(CH_3)_3Si]_2O$ adsorption at τ 9.93 (present initially) and the GeH_4 absorption at τ 6.85[26] (observed after 1.4 days) steadily increased and were the only signals remaining in the spectrum after 18.5 days. The absorptions from GeH_3SSiH_3 (14% by volume in deuteriocyclohexane with TMS added) slowly decreased over a 27-day test period although weak absorptions from the compound were still observed at the end of the test. An absorption from $(GeH_3)_2S$ at τ 5.38[17] slowly increased until a GeH_4 signal was observed after 9.9 days. After this, the $(GeH_3)_2S$ absorption remained constant. Signals from $(SiH_3)_2S$ at τ 5.65[27] and GeH_4 slowly increased in intensity over the test period. A sample of $GeH_3SSi(CH_3)_3$ (14% by volume in deuteriocyclohexane with C_6H_{12} added) showed a gradual decrease in the absorptions of $GeH_3SSi(CH_3)_3$ and a gradual increase in absorptions assigned to $[(CH_3)_3Si]_2S$ (τ 9.67) and $(GeH_3)_2S$ (τ 5.38) over a 3-day period. After that time no further change in the nmr spectrum was detected.

Results and Discussion

Two groups of investigators have investigated the synthesis of the mixed sulfide GeH_3SSiH_3. Drake and Riddle first detected the compound among the products formed by subjecting a mixture of SiH_4, GeH_4, and H_2S to a silent electrical discharge.[18] Identification was made solely by an nmr analysis of the product mixture. Ebsworth and coworkers reported that the compound was formed in the reaction of NH_4SSiH_3 with GeH_3Br, but separation attempts were unsuccessful owing to the tendency for the compound to decompose.[28] In the present work, we have investigated the synthesis of SiH_3SGeH_3 by the equimolar exchange reaction involving $(SiH_3)_2S$ and GeH_3Cl (eq 1). Exchange reactions of this type usually occur

$$GeH_3Cl + (SiH_3)_2S \rightarrow GeH_3SSiH_3 + SiH_3Cl \qquad (1)$$

under very mild conditions and we felt that a synthesis based on this method should be appropriate to try, particularly if the stability of the compound were questionable. The course of such a reaction would be consistent with other previously reported exchange reactions involving silyl and germyl compounds in which the lighter (or at least not much heavier) more electronegative substituent of the pair becomes bound to silicon.[29] Consistent with this concept is our observation that pure $(GeH_3)_2S$ could be conveniently obtained by the exchange that GeH_3Cl undergoes with $(SiH_3)_2S$ (2:1 molar ratio) (eq 2). However, it was not clear whether or not an

$$2GeH_3Cl + (SiH_3)_2S \rightarrow (GeH_3)_2S + 2SiH_3Cl \qquad (2)$$

equimolar exchange reaction could be used to produce the mixed sulfide. A previously reported nmr study of the equimolar exchange reaction involving GeH_3I and $(SiH_3)_3P$ indicated that mixed silyl(germyl)phosphines were not formed.[30]

Our study indicated that the equimolar exchange reaction involving GeH_3Cl and $(SiH_3)_2S$ does proceed at room temperature in the absence of a solvent according to eq 1. From the amount of SiH_3Cl recovered the reaction is quantitative. We were not able to characterize the mixed sulfide in the liquid phase owing to its apparent instability. Unequivocal evidence for the formation of the compound was obtained from the compound's characteristic two-quartet proton nmr spectrum.[18]

The decomposition of SiH_3SGeH_3 appears to involve a straightforward disproportionation, at least initially (eq 3).

$$2SiH_3SGeH_3 \rightarrow (SiH_3)_2S + (GeH_3)_2S \qquad (3)$$

Small peaks attributed to $(GeH_3)_2S$ and $(SiH_3)_2S$ were detected in the initial nmr spectrum of the compound, and these

Table I. Vibrations of Germyl Silyl Sulfide

Vibration	Symmetry class a'	a''
SiH_3 asym str	ν_1	ν_{14}
SiH_3 sym str	ν_2	
GeH_3 asym str	ν_3	ν_{15}
GeH_3 sym str	ν_4	
SiH_3 asym def	ν_5	ν_{16}
SiH_3 sym def	ν_6	
GeH_3 asym def	ν_7	ν_{17}
GeH_3 sym def	ν_8	
SiH_3 rock	ν_9	ν_{18}
GeH_3 rock	ν_{10}	ν_{19}
Si–S str	ν_{11}	
Ge–S str	ν_{12}	
Si–S–Ge bend	ν_{13}	
SiH_3 torsion		ν_{20}
GeH_3 torsion		ν_{21}

gradually increased almost immediately in intensity relative to peaks assigned to GeH_3SSiH_3. After keeping the nmr sample for about 10 days at room temperature, an analysis revealed the presence of some GeH_3SSiH_3, but the two symmetrical sulfides constituted the major part of the sample. When a neat sample of GeH_3SSiH_3 was allowed to decompose at room temperature for 3 days, an uncharacterized brown solid formed together with a noncondensable gas (presumed to be hydrogen) and a mixture of $(SiH_3)_2S$, $(GeH_3)_2S$, GeH_4, and some GeH_3SSiH_3. After 5 days under these conditions, none of the GeH_3SSiH_3 survived. The decomposition is actually slow enough to tolerate under normal conditions involving vacuum-line experiments, however, once it starts, it is impossible to remove $(SiH_3)_2S$ from the mixed sulfide by vacuum-line methods.

Germyl silyl sulfide appears to be considerably more stable in the gas phase than in the liquid phase. This conclusion is based on the observation that the gas-phase infrared spectrum of a sample that was rich in GeH_3SSiH_3 remained essentially unchanged after keeping the sample in the gas cell for 7.5 hr at room temperature. The presence of $(GeH_3)_2S$ is particularly easy to recognize and monitor in the infrared spectrum by the ν(GeS) band at 412 cm^{-1}.[16] We obtained the infrared spectrum of a freshly prepared sample of GeH_3SSiH_3 which proved to be sufficiently pure to obtain most of the desired assignments. Assuming that silyl germyl sulfide has a bent heavy-atom skeleton as do $(SiH_3)_2S$ and $(GeH_3)_2S$, the only element of symmetry the molecule could possess is a mirror plane. The molecule would then belong to point group C_s of which both the a' and a'' species are singly degenerate and infrared active. Silyl germyl sulfide is a nine-atom molecule and would therefore have 21 infrared-active fundamental vibrations. Approximate descriptions of the fundamental vibrations of silyl germyl sulfide are given in Table I. The observed absorption frequencies and tentative assignments are listed in Table II.

Faced with the instability of the desired mixed hydride derivative containing the Ge–S–Si linkage, we attempted the synthesis of the partially substituted derivative $GeH_3SSi(CH_3)_3$. Organic groupings usually impart a certain degree of stability to various group IV hydride derivatives. An attempt was made to prepare the mixed sulfide by the equimolar exchange interaction of GeH_3Cl with $[(CH_3)_3Si]_2S$; however a spectroscopic analysis indicated that the exchange was not complete enough for preparative purposes even after the reaction mixture was allowed to stand at room temperature for 5 days.

$$[(CH_3)_3Si]_2S + GeH_3Cl \leftrightarrows GeH_3SSi(CH_3)_3 + (CH_3)_3SiCl \qquad (4)$$

Table II. Infrared Absorption Frequencies of Germyl Silyl Sulfide[a]

Freq, cm^{-1}	Assignment	Freq, cm^{-1}	Assignment
3115 vw	$\nu_2 + \nu_{16}, \nu_2 + \nu_5$	872 w	ν_{17}, ν_7
2188 sh	ν_{14}, ν_1	838 s	ν_8
		827 s	
2180 s	ν_2		
2104 m	ν_{15}, ν_3, ν_4	638 w	ν_9
1873 vw	$2\nu_{16}, 2\nu_5$	620 w	ν_{18}
1275 vw	$2\nu_9$	581 w	ν_{10}
1222 vw	$\nu_9 + \nu_{10}$	571 w	ν_{19}
1158 vw	$2\nu_{10}, \nu_9 + \nu_{11}$	531 m	ν_{11}
1098 vw	$\nu_{19} + \nu_{11}$	517 m	
1015 sh	$\nu_{18} + \nu_{12}$		
938 vs	ν_{16}, ν_5	405 w	ν_{12}
919 vs	ν_6	393 w	
911			

[a] Assignments made with the aid of the published results for the related compounds disilyl sulfide[12] and digermyl sulfide.[16] Abbreviations and arbitrary designations used in this table: s, strong; m, medium; w, weak; v, very; sh, shoulder.

A much more satisfactory synthesis involves the equimolar exchange of GeH_3F with $[(CH_3)_3Si]_2S$ (eq 5). Under the conditions described, the reaction appears to produce the mixed sulfide quantitatively.

$$[(CH_3)_3Si]_2S + GeH_3F \rightarrow GeH_3SSi(CH_3)_3 + (CH_3)_3SiF \qquad (5)$$

As in the case of GeH_3SSiH_3, the compound readily underwent disproportionation in the liquid phase forming $[(CH_3)_3Si]_2S$ and $(GeH_3)_2S$ (eq 6). The fact

$$2GeH_3SSi(CH_3)_3 \rightarrow (GeH_3)_2S + [(CH_3)_3Si]_2S \qquad (6)$$

that $GeH_3SSi(CH_3)_3$ and the two symmetric sulfides derived therefrom had similar volatilities prevented us from isolating and characterizing the pure mixed sulfide. The formation of the desired $GeH_3SSi(CH_3)_3$ was revealed by an nmr spectrum of the products of the reaction.

Qualitative stability studies indicated that $GeH_3SSi(CH_3)_3$ is considerably more stable in the vapor phase than in the liquid phase. Thus, we were able to obtain a satisfactory infrared spectrum for the compound, although trace amounts of $[(CH_3)_3Si]_2S$ and $(GeH_3)_2S$ were detected in the spectrum. Assuming normal bond angles, the only symmetry element the molecule could possess is a mirror plane in which case it would belong to point group C_s. Both the a' and a'' species of point group C_s are singly degenerate so the molecule would have 48 infrared-active fundamentals. Due to the complexity of the vibrational spectrum, a complete assignment was not attempted. The observed infrared frequencies and tentative assignments for the mixed sulfide are given in Table III and compared with corresponding data for $[(CH_3)_3Si]_2S$ and $(GeH_3)_2S$. It is noted that a good correlation exists between the vibrational frequencies of the mixed sulfide and the analogous modes of the corresponding symmetric sulfides.

The use of an exchange reaction involving equimolar quantities of $[(CH_3)_3Si]_2O$ and GeH_3F to produce $(CH_3)_3SiOGeH_3$ was not attempted owing to the report that exchange involving these two components is unsatisfactory.[30] The synthesis of the compound was attempted by the reaction of solid $(CH_3)_3SiOLi$ with GeH_3Cl (eq 7). Nmr and mass

$$(CH_3)_3SiOLi + GeH_3Cl \rightarrow GeH_3OSi(CH_3)_3 + LiCl \qquad (7)$$

spectral data on the material produced in the reaction indicate that the mixed ether is formed, but it was soon apparent that the compound readily undergoes disproportionation in the liquid phase.

$$2(CH_3)_3SiOGeH_3 \rightarrow [(CH_3)_3Si]_2O + (GeH_3)_2O \qquad (8)$$

It is important to note that in order to obtain reasonably pure samples of $GeH_3OSi(CH_3)_3$ by our procedure, it is necessary to remove the product from the reaction vessel at low temperatures, as soon as it is formed. If the product is allowed to remain in the vessel during the reaction, low yields of very impure material result.

As in the case of the mixed sulfides under investigation, we

Table III. Infrared Absorption Frequencies of Hexamethyldisilyl Sulfide, Germyl Trimethylsilyl Sulfide, and Digermyl Sulfide[a]

Vibration	$(CH_3)_3$-SiSSi-$(CH_3)_3$[b]	GeH_3-SSi-$(CH_3)_3$	GeH_3SGeH_3[c]
$\nu_{as}(CH_3)$	2960 m	2968 m	
$\nu_s(CH_3)$	2900 w	2906 w	
$\nu_{as}(GeH_3)$		2104 sh	2110 s
$\nu_s(GeH_3)$		2089 s	2097 s
$\delta_{as}(CH_3)$	1402 w	1405 w	
$\delta_s(CH_3)$	1256 s	1257 s	
$\rho(CH_3)$	847 vs	$\left.\begin{array}{l}\\ \\ \end{array}\right\}$851 br, s	
$\delta_{as}(GeH_3)$			872 sh
			849 s
$\delta_s(GeH_3)$		827 vs	$\left.\begin{array}{l}823\text{ R}\\816\text{ P}\end{array}\right\}$ vs
$\nu_{as}(SiC_3)$	756 m	755 w	
	690 w	690 w	
$\nu_s(SiC_3)$	627 s	634 m	
$\rho(GeH_3)$		581 w	577 m
			556 m
$\nu(SiS)$	495 s	461 s	
	438 w		
$\nu(GeS)$		401 w	412 s
			382 w

[a] Abbreviations and arbitrary designations used in this table: ν_{as}, asymmetric stretching mode; ν_s, symmetric stretching mode; δ_{as}, asymmetric deformation mode; δ_s, symmetric deformation mode; ρ, rocking mode; s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. All spectral values are for the vapor phase. [b] Gas-phase spectrum obtained in this laboratory; assignments correlated with those for the liquid phase spectrum in ref 13. [c] Reference 16.

Table IV. Infrared Absorption Frequencies of Hexamethyldisiloxane, Germyl Trimethylsilyl Ether, and Digermyl Ether[a]

Vibration	$(CH_3)_3$-SiOSi-$(CH_3)_3$[b]	$GeH_3OSi(CH_3)_3$	GeH_3OGeH_3[c]
$\nu_{as}(CH_3)$	2960 s	2972 sh	
		2956 s	
$\nu_s(CH_3)$	2905 m	2897 m	
		2855 m	
$\nu_{as}(GeH_3)$			2120 sh
		2110 sh	2112 s
$\nu_s(GeH_3)$		2095 s	2084 s
$\delta_{as}(CH_3)$	1445 w	1443 w	
	1408 w	1410 w	
$\delta_s(CH_3)$	1260 s	1255 s	
$\delta_{as}(GeH_3)$			937 w
			928 w
		844 br, vvs	850 sh
$\delta_s(GeH_3)$		807 sh	798 vs
		790 sh	784 vs
$\rho(CH_3)$	850 s	752 m	
$\nu_{as}(SiC_3)$	759 m	666 sh	
	688 m	645 br, m	
$\rho(GeH_3)$			674 m
$\nu_s(SiC_3)$	616 m		
$\nu(SiO)$	1070 vs	1005 vs	
	506 vw		
$\nu(GeO)$			882 br, m
		502 m	452 br, w

[a] Abbreviations and arbitrary designations used in this table: ν_{as}, asymmetric stretching mode; ν_s, symmetric stretching mode; δ_{as}, asymmetric deformation mode; δ_s, symmetric deformation mode; ρ, rocking mode; s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. All spectral values for vapor phase. [b] Gas-phase spectrum obtained in this laboratory; assignments correlated with those for liquid-phase spectrum in ref 13. [c] Reference 16; S. Cradock, *J. Chem. Soc. A*, 1426 (1968).

found that $GeH_3OSi(CH_3)_3$ is considerably more stable in the vapor phase than in the liquid phase with respect to disproportionation. As a result, we were able to obtain good vapor-phase infrared spectra for the compound. Owing to the complexity of the vibrational spectrum, a complete assignment was not made. The observed frequencies and tentative assignments for $GeH_3OSi(CH_3)_3$ are given in Table IV and compared with corresponding data for $[(CH_3)_3Si]_2O$ and $(GeH_3)_2O$. It is noted that the data for the mixed ether correlate well with the analogous data for the two symmetric ethers.

Each of the three silyl–germyl mixed group IVa compounds investigated in this work underwent disproportionation to form the corresponding symmetric ethers or sulfides in the liquid phase and in cyclohexane. In each case, decomposition of the neat liquid was more rapid than decomposition in solution and in the gas-phase all three compounds exhibited excellent stability over a period of several hours. Of the three derivatives investigated in this work, $GeH_3OSi(CH_3)_3$ underwent the most rapid decomposition. After 3 days at room temperature, a neat liquid sample had completely decomposed to form $[(CH_3)_3Si]_2O$, GeH_4, H_2, and a solid residue. The process under these conditions most likely involves disproportionation initially (eq 8), followed by the decomposition of $(GeH_3)_2O$. A time period of 5 days at room temperature was required for a similar sample of GeH_3SSiH_3 to decompose completely. The most stable mixed group VIa derivative investigated in this work is $GeH_3SSi(CH_3)_3$. After 10 days at room temperature, a liquid sample of $GeH_3SSi(CH_3)_3$ contained the mixed sulfide and the two symmetric sulfides.

Liquid-phase decomposition is a common problem encountered in working with certain derivatives of silicon and germanium hydrides. In the present work we have shown that hydride derivatives containing the Si–O–Ge and Si–S–Ge linkages present serious survival problems owing to the ease with which they disproportionate (eq 9). No stability problems of this type have been reported for the analogous completely substituted triorganosilyl triorganogermyl derivatives.[31] The mode of decomposition for the silicon- and GeH_3-containing mixed ether and sulfide is quite different from that of hydride derivatives that contain the heteratom Ge–O–C and Ge–S–C linkages. For example, the main thermal decomposition products of CH_3OGeH_3 at 0° are CH_3OH, GeH_4, uncharacterized solids, and possibly $(GeH_3)_2O$.[32] The compound CH_3SGeH_3 is reasonably stable thermally; a sample was held for 7 days at room temperature with no apparent decomposition.[17]

$$2R_3SiXGeH_3 \rightarrow (R_3Si)_2X + (GeH_3)_2X \qquad (9)$$

$$X = S, R = H, CH_3; X = O, R = CH_3$$

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Registry No. GeH_3SSiH_3, 29770-45-4; $(GeH_3)_2S$, 18852-54-5; $GeH_3SSi(CH_3)_3$, 52810-58-9; $GeH_3OSi(CH_3)_3$, 52810-59-0; $GeH_3OSi(CH_3)_3$, 52810-59-0; GeH_3Cl, 13637-65-5; $(SiH_3)_2S$, 16544-95-9; GeH_3F, 13537-30-9; $[(CH_3)_3Si]_2S$, 3385-94-2; $(CH_3)_3SiOLi$, 2004-14-0.

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Spectroscopic Study of Telluric Acid and Selenic Acid in Hydrogen Fluoride and the Hydrolysis of Tellurium Hexafluoride

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The equilibrium $Te(OH)_6 + nHF \rightleftharpoons Te(OH)_nF_{6-n} + nH_2O$ has been studied, mainly by ^{19}F nmr spectroscopy. In the solvolysis of $Te(OH)_6$ in HF, products up to $n = 3$ have been identified, while in the hydrolysis of TeF_6 products with $n = 0$–5 have been observed. The stereochemical configuration of most of the species has been determined. Solvolysis of selenic acid in HF leads to pentafluoroorthoselenic acid and two other products, one of which is probably $HSeO_3F$.

Introduction

The chemistry of pentafluoroorthotelluric acid and of pentafluoroorthoselenic acid has received considerable attention after their initial syntheses.[1,2] Among its many chemical properties, pentafluoroorthotelluric acid dissolves in water to give a strongly acidic solution which hydrolyzes to mixtures of other fluorotelluric acids.[3] Some of these fluorotelluric acids have been isolated by chromatographic separation of a mixture obtained by dissolving telluric acid in 40% hydrofluoric acid.[4] In such mixtures the following equilibria obtain

$$Te(OH)_6 + nHF \rightleftharpoons Te(OH)_nF_{6-n} + nH_2O$$

but only acids with $n = 2$–6 were thus obtained on the developed chromatogram, and their R_f values were determined.[4] A number of salt derivatives of the di- and tetrafluorotelluric acids were isolated. Nothing is known about their structures, but it was assumed that in each case the symmetric trans complex is involved.[4,30]

It has been our experience that isolation or separation of products from such reaction mixtures does not necessarily throw light on the nature of the species in solution, and we have therefore investigated several systems by studying their fluorine nmr spectra or the Raman spectra of the solutions directly. We have found, for instance, that solutions of iodate,[5] perrhenate,[5] pertechnetate,[6] and periodate[7] in anhydrous hydrogen fluoride (AHF) lead to solutions of iodine pentafluoride, perrhenyl fluoride, pertechnetyl fluoride, and tetrafluoroorthoperiodic acid, respectively. The system $Te(OH)_nF_{6-n}$–HF has now been investigated by fluorine nmr and partially by Raman spectroscopies. In order to achieve maximum ligand exchange, large amounts of HF would be required. The resulting solutions are too dilute to lend themselves readily to spectroscopic investigation. We have therefore also approached the equilibrium from the opposite direction by controlled hydrolysis of tellurium hexafluoride. Parallel experiments with selenic acid and selenium hexafluoride were also carried out.

Experimental Section

Materials. Orthotelluric acid was prepared by the oxidation of tellurium dioxide (Fluka, practical grade) with potassium permanganate.[8] Raman spectra of aqueous solutions of the product were in agreement with those cited in the literature.[9,10] Selenic acid was obtained in the form of a concentrated solution from BDH. Tellurium hexafluoride and selenium hexafluoride were prepared from the elements and purified by fractional distillation until vibrational spectra attested to their purity. Anhydrous hydrogen fluoride (AHF) was obtained from a still previously described.[11]

Apparatus. High-resolution fluorine nmr spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz. Spectra were calibrated by the method of side bands using a Hewlett-Packard Model 4204A oscillator. The side band frequency could be varied so as not to interfere with other signal lines. Chemical shifts are reported with respect to CCl_3F used as an external standard, and in the case of proton nmr spectra with respect to an external TMS standard. Some of the $Te(OH)_nF_{6-n}$ species observed, having sets of nonequivalent fluorine atoms, displayed rather complex spectra. The parameter determining the exact appearance of these spectra is $R = J_{AB}/\delta_{AB}$, where J_{AB} is the coupling constant between axial and equatorial fluorines and δ_{AB} the chemical shift difference between these fluorines expressed in hertz. The AB_4 spectra assigned to $HOTeF_5$ were analyzed by the method of Harris and Packer.[12] A useful, brief description of the procedure has also been given by Seppelt.[13] Spectra of the types AB_2 and A_2B_2 were analyzed according to procedures given by Bovey.[14] The latter also gives useful calculated line spectra enabling visual identification of complex spectra.

Raman spectra were obtained in Kel-F or Teflon FEP tubes on an apparatus previously described.[7] Raman lines of the plastic container were eliminated by positioning the tube so that the bright spots created by the laser beam entering and exiting the tube were masked by the slit height attenuator. Spectra were calibrated by reference to emission lines of neon and are accurate to ±2 cm^{-1} on the sharp bands.

Procedure. Samples were prepared in $^3/_{16}$-in. o.d. Kel-F tubes by