N.M.R. Studies of Mixed Group 4/Group 6 Hydrides

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The equilibria

$$(MH_3)_2E + H_2E \rightleftharpoons 2MH_3EH \ (E = S, Se, Te; \ M = Si, Ge)$$

have been studied by ^{1}H nuclear magnetic resonance spectroscopy. The spectra of the new compounds MH_3EH (E = Se, Te; M = Si: E = S, Se, Te; M = Ge) are reported, including satellites due to ^{29}Si, ^{77}Se and ^{125}Te at natural abundance. The ^{125}TeH coupling constant in H_2Te is also reported for the first time.

Of the monosilyl derivatives of the group 6 hydrides, only SiH_3SH[1, 2] has been prepared previously; none of the corresponding germyl compounds has been reported. We present here n.m.r. evidence for the existence of SiH_3SeH, SiH_3TeH, GeH_3SH, GeH_3SeH and GeH_3TeH.

EXPERIMENTAL

All manipulations were performed in conventional Pyrex vacuum systems with the rigorous exclusion of air and moisture. $(SiH_3)_2Te$ was prepared by reaction of silyl bromide with Li_2Te in dimethyl ether at −96°C [3]; $(SiH_3)_2S$, $(SiH_3)_2Se$ and $(GeH_3)_2S$ were prepared similarly. $(GeH_3)_2Se$ and $(GeH_3)_2Te$ were prepared from the corresponding silyl compounds by exchange with germyl bromide.[4] H_2S was prepared from CaS and acetic acid, HCl from NaCl and conc. H_2SO_4, and H_2Se from water and Al_2Se_3. All the compounds were purified by repeated fractional condensation *in vacuo*. A.R. chloroform was further purified by distillation from alumina which had been heated *in vacuo*. All the n.m.r. spectra were recorded as dilute solutions in chloroform using a Varian Associates HA 100 spectrometer and calibrated with a Muirhead-Wigan decade oscillator. Chemical shifts in the sulphide and selenide spectra were measured relative to chloroform and converted to the τ scale by adding 2·76; all shifts in the telluride spectra (including the above value for chloroform) were measured relative to tetramethylsilane. All the spectra were recorded at room temperature except where otherwise indicated. The sulphide and selenide mixtures were prepared from equimolar quantities of $(MH_3)_2E$ and H_2E (M = Si, Ge and E = S, Se) and the tellurium compounds by mixing equimolar quantities of $(MH_3)_2Te$ and HCl in the n.m.r. tubes.

RESULTS AND DISCUSSION

CHEMICAL SHIFTS

The MH_3—E (E = S, Se, Te) proton chemical shifts presented here follow the general trend[7–10] of increasing τ value as groups 5, 6 and 7 of the periodic table are descended. This is probably related to an increase in diamagnetic anisotropy of the Si—E and Ge—E bonds, which is consistent with the larger differences for E = S, Se, Te in the germyl as opposed to silyl derivatives. This also accounts for the observed increases in EH proton chemical shift in the series $GeH_3EH \geqslant SiH_3EH > EH_2$ and $-TeH > -SeH > -SH$. In view of the influence of possible conformational differences (exemplified by the electron diffraction study of $(SiH_3)_2Se$)[11] it would have been difficult to predict the variations of $\tau(MH)_3$ in MH_3EH relative to $(MH_3)_2E$.

TABLE 1.—CHEMICAL SHIFTS

	$\tau(MH_3)$p.p.m.	$\tau(EH)$p.p.m.
H_2S	—	9·25 ± 0·01
H_2Se	—	11·25 ± 0·01
H_2Te	—	15·50 ± 0·01[a]
SiH_3SH	5·69 ± 0·01[b]	10·12 ± 0·01[b]
SiH_3SeH	5·91 ± 0·01	12·28 ± 0·01
SiH_3TeH	6·23 ± 0·01	17·46 ± 0·01[c]
GeH_3SH	5·48 ± 0·01	10·25 ± 0·01
GeH_3SeH	5·81 ± 0·01	12·52 ± 0·01
GeH_3TeH	6·38 ± 0·01	17·44 ± 0·01
$(SiH_3)_2S$	5·65 ± 0·01	—
$(SiH_3)_2Se$	5·91 ± 0·01	—
$(SiH_3)_2Te$	6·33 ± 0·01	—
$(GeH_3)_2S$	5·33 ± 0·01	—
$(GeH_3)_2Se$[d]	5·68 ± 0·01	—
$(GeH_3)_2Te$[d]	6·34 ± 0·01	—

(*a*) 15·31 ± 0·01 at −30°C; (*b*) ref. (2); (*c*) at −30°C; (*d*) ref. (4).

COUPLING CONSTANTS

The directly bonded $^{125}Te—H$ satellites could not be detected in H_2Te, $HTeSiH_3$ and $HTeGeH_3$ at room temperature, despite the observation of multiplets due to a long H . . . H coupling in the latter two molecules. The satellites could be observed in the spectra recorded at *ca.* −30°C, so we attribute their absence at room temperature to exchange of hydrogen atoms bonded to tellurium. Since $^{125}Te—H$ is exchanging with a large excess of hydrogen atoms bonded to (effectively) non-magnetic tellurium, which have a different " effective chemical shift ", the satellites should be much broader than the main resonance, as observed in H_2Se[12]; at room temperature the mean lifetimes of the Te—H bonds must be intermediate between the values

TABLE 2.—COUPLING CONSTANTS

	$^1J(^{29}Si—H)$,Hz	$^1J(E—H)$,Hz	$^2J(E—H)$,Hz	$^3J(H—H)$,Hz
H_2Se	—	59·4 ± 0·5	—	—
H_2Te	—	59 ± 2[a]	—	—
CH_3SH	—	—	—	7·6 ± 0·2[b]
SiH_3SH	224 ± 1	—	—	4·7 ± 0·1[c]
SiH_3SeH	225 ± 1	51·0 ± 0·1	15·4 ± 0·2	5·0 ± 0·1
SiH_3TeH	224 ± 1	57·6 ± 0·1[a]	32·4 ± 0·2	4·8 ± 0·1
GeH_3SH	—	—	—	4·1 ± 0·1
GeH_3SeH	—	41·0 ± 0·1	14·4 ± 0·2	4·3 ± 0·1
GeH_3TeH	—	51·9 ± 0·3[a]	22·5 ± 0·3	4·4 ± 0·2
$(CH_3)_2Se$	—	—	+10·5 ± 0·2[d]	—
$(CH_3)_2Te$	—	—	−20·7 ± 0·2[d]	—
$(SiH_3)_2Se$	225 ± 1	—	14·9 ± 0·2	—
$(SiH_3)_2Te$	224 ± 1	—	27·4 ± 0·2	—
$(GeH_3)_2Se$	—	—	12·3 ± 0·1[e]	—
$(GeH_3)_2Te$	—	—	19·4 ± 0·2[e]	—

(*a*) at −30°C; (*b*) ref. (5); (*c*) ref. (2); (*d*) ref. (6); (*e*) ref. (4).

required for collapse of ^{125}Te—H coupling ($J\sim60$ Hz) and H . . . H coupling ($J\sim4$ Hz).

McFarlane[6] has shown that the reduced ^{77}Se . . . H and ^{125}Te . . . H coupling constants in $(CH_3)_2Se$ and $(CH_3)_2Te$ are positive (relative to $J(^{13}CH)$); the relative values for $J(^{77}Se\ldots H)$ in $(CH_3)_2Se$, $(CH_3)_2Se_2$ and $(CH_3)_3Se^+I^-$ were consistent with a model[13] dominated by changes in hybridization of the selenium, and not by changes in effective nuclear charge.[14] The observed bond angles in $(SiH_3)_2S$[15] and $(SiH_3)_2Se$[11] provide no evidence for "$(p\rightarrow d)$ π-bonding", but not do preclude "$(s\rightarrow d)\sigma$-bonding" from E to Si, which we tentatively invoked[16] to account for the weak base strength and poor nucleophilic character of $(SiH_3)_3P$ relative to $(CH_3)_3P$. This mechanism for an increase in *s* character (on E) in the bonding accounts for the observation that all the values of $|\,^1J(EH)\,|$ and $|\,^2J(E\ldots H)\,|$ reported here are greater in the silyl than in the corresponding methyl or germyl compounds, and enables the prediction to be made that the corresponding reduced coupling constants will be positive in the silyl compounds.

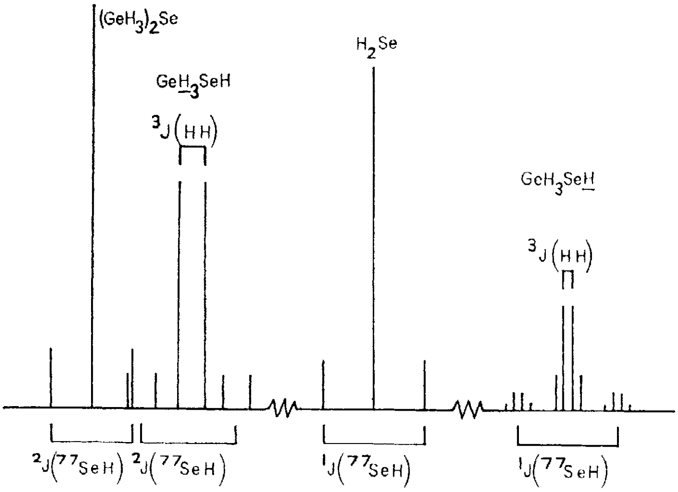

FIG. 1.—Diagram (not to scale) of n.m.r. spectrum of equilibrium mixture of $(GeH_3)_2Se + H_2Se \rightleftharpoons 2GeH_3SeH$

EQUILIBRIUM CONSTANTS

Whereas the $(SiH_3)_2S$ and H_2S mixture required several weeks to come to equilibrium, and the $(GeH_3)_2S$ and H_2S mixture several days, the selenides and tellurides had reached equilibrium within a few hours. The values obtained for the equilibrium constant *K* were: 0·3, 0·5, 0·9($(H_3Si)_2S$,Se,Te) and 0·35, 0·6, 0·95 ($(GeH_3)_2S$,Se,Te resp.) (all estimated errors ±0·1), where *K* is defined by

$$K = [MH_3EH]^2/[(MH_3)_2E][H_2E]$$

These values are approximate due to difficulties in integrating the n.m.r. multiplets; they are significantly less than the random value of 4, and exhibit the consistent trends $K(Ge) > K(Si)$ and $K(Te) > K(Se) > K(S)$. However, H-bonding by the chloroform solvent would favour the formation of stronger bases, hence, at least in part, accounting for these observations.

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