## Electric Discharge Reactions of Silane and Germane with Some Volatile **Group VI Species**

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The action of a silent electric discharge on equimolar mixtures of the following hydrides:  $SiH_4/H_2S$ ,  $SiH_4/H_2Se$ , GeH<sub>4</sub>/H<sub>2</sub>S, GeH<sub>4</sub>/H<sub>2</sub>Se, SiH<sub>4</sub>/GeH<sub>4</sub>/H<sub>2</sub>S, SiH<sub>4</sub>/GeH<sub>4</sub>/H<sub>2</sub>Se, SiH<sub>4</sub>/MeSH, and GeH<sub>4</sub>/MeSH, has been investigated. Analysis of the reaction products by <sup>1</sup>H n.m.r. and mass spectroscopy indicates the formation of the previously known mixed and ternary hydrides: SiH<sub>3</sub>SH, (SiH<sub>3</sub>)<sub>2</sub>S, SiH<sub>3</sub>SeH, (SiH<sub>3</sub>)<sub>2</sub>Se, GeH<sub>3</sub>SH, (GeH<sub>3</sub>)<sub>2</sub>S, GeH<sub>3</sub>SeH, (GeH<sub>3</sub>)<sub>2</sub>Se, MeSSiH<sub>3</sub>, and MeSGeH<sub>3</sub>. The new compounds SiH<sub>3</sub>SGeH<sub>3</sub> and SiH<sub>3</sub>SeGeH<sub>3</sub> are obtained from discharges of the ternary mixtures.

THE electric discharge has been used in the synthesis of the higher binary silanes and germanes,  $M_n H_{2n+2}$  (M = Si or Ge; n = 2-9)<sup>1</sup> and in the preparation of mixed Group IV-Group IV hydrides, e.g. SiH<sub>3</sub>GeH<sub>3</sub>,<sup>2</sup> or Group IV-Group V hydrides, e.g. GeH<sub>3</sub>AsH<sub>2</sub>.<sup>3</sup> Å degree of specificity has been claimed for some of these reactions indicating a favoured reaction path.<sup>4,5</sup> Mercury-sensitised photolysis of hydride mixtures has also been used to produce mixed species via radical combination.6 Sulphur atoms, produced in a discharge from COS or  $CS_2$ , insert into  $\equiv C-H$  bonds to give  $\equiv C-SH.^7$ 

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<sup>2</sup> E. J. Spanier and A. G. MacDiarmid, Inorg. Chem., 1963, 2, 215. <sup>3</sup> J. E. Drake and W. L. Jolly, Chem. and Ind., 1962, 1470.

We report the result of subjecting mixtures of SiH<sub>4</sub> or  $GeH_4$  with  $H_2S$ , MeSH, or  $H_2Se$  to an ozoniser-type silent electric discharge. The products were initially identified by <sup>1</sup>H n.m.r. spectroscopy and the results confirmed by i.r. and mass spectroscopy.

## EXPERIMENTAL

Apparatus.—The experiments were carried out in a conventional Pyrex glass vacuum line fitted with greaseless

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<sup>6</sup> G. A. Gibbon, Y. Rousseau, C. H. Van Dyke, and G. J. Mains, *Inorg. Chem.*, 1966, 5, 114. <sup>7</sup> O. P. Strausz and H. E. Gunning, J. Amer. Chem. Soc.,

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3135

stopcocks (Springham; Viton A diaphragm). The discharge unit <sup>1</sup> consists of an ozoniser, following trap, surge bulb, and circulating pump (total volume 1900 ml). Series of 1 h discharges were run at 13 kV with the discharge tube maintained at 0°. After each run hydrogen was pumped off and the reactants returned to the discharge system after passage through a  $-95^{\circ}$  trap which retained the products. No separation was attempted between runs involving MeSH because its volatility is similar to that of some of the products. Equimolar mixtures of gases were used such that the pressure in the discharge system was between 10-30 cm. As previous workers have reported,<sup>8</sup> the discharge reaction was considerably 'quenched' at higher pressures, notably with SiH<sub>4</sub>/H<sub>2</sub>S mixtures where 20 cm was the optimum pressure. On average each discharge produced ca. 10% decomposition of starting materials.

The products were identified principally from their <sup>1</sup>H n.m.r. spectra. The chemical shift (all values quoted are in p.p.m. to low field of tetramethylsilane) and spin-spin coupling data are well documented and characteristic, especially for the 'mixed' hydrides. I.r. and mass spectroscopy were used to confirm the interpretation of the n.m.r. spectra. For the Group IV hydrides  $M_x H_{2x+2}$  and  $M_xM'_yH_{2(x+y)+2}$  (M = Si or Ge; M' ( $\neq$  M) = Si or Ge), and the Group VI compounds  $Me_2S_x$  (x = 1 or 2) which have overlapping resonance regions in the n.m.r. spectrum, mass spectroscopy was particularly useful.

The <sup>1</sup>H n.m.r. spectra were recorded in sealed tubes (ca. 2 mm o.d.) on a Jeol C60HL high-resolution spectrometer. I.r. spectra were recorded on Beckman IR 10 and IR 12 spectrometers in gas cells (5 cm path-length) fitted with potassium bromide windows and mass spectra on an AEI MS 10 instrument.

Starting Materials.-Commercial silane and germane were used after non-condensable gas (hydrogen) had been pumped off at  $-196^{\circ}$ . Hydrogen sulphide <sup>9</sup> and selenide <sup>10</sup> were prepared from the hydrolysis of freshly made aluminium sulphide and selenide alloy, and purified by repeated distillation on the vacuum line. Commercial methanethiol was used as supplied.

Discharge Reactions.— $SiH_4/H_2S$ . The products from a series of 1 h discharges were analysed from their <sup>1</sup>H n.m.r. spectra which showed resonances at 3.25 (Si<sub>2</sub>H<sub>6</sub>), 3.3 $(\mathrm{Si_3H_8}),^{11}$  3·3 and 3·4 (iso- and n-Si\_4H\_{10}),^{12} 4·29 and -0.07(SiH<sub>3</sub>SH), and 4.35 p.p.m. [(SiH<sub>3</sub>)<sub>2</sub>S].<sup>13</sup> The ratio of higher silanes to sulphur-containing product species was ca. 1:1.

The mass spectrum gave parent peaks at m/e 64 (Si<sub>6</sub>H<sub>6</sub>), 96 [(SiH<sub>3</sub>)<sub>2</sub>S], and 126 (Si<sub>4</sub>H<sub>10</sub>) (all unipositive ions).

 $SiH_4/H_2Se$ . The products from a series of 1 h discharges gave resonances in the <sup>1</sup>H n.m.r. spectrum at 4.10 and -2.33p.p.m. (SiH<sub>3</sub>SeH), and 4·10 p.p.m. [(SiH<sub>3</sub>)<sub>2</sub>Se],<sup>13</sup> as well as those attributable to the higher silanes  $Si_2H_6$ ,  $Si_3H_8$ , Si<sub>4</sub>H<sub>10</sub>.<sup>11,12</sup> The spectrum of <sup>29</sup>SiH<sub>3</sub>SeSiH<sub>3</sub>', the species observed in the 29Si satellite region of (SiH<sub>3</sub>)<sub>2</sub>Se, displayed long-range, H–(Si–Se–Si–)H', coupling ( $|J_{\rm HH'}| 0.63$  Hz) with

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 <sup>14</sup> E. A. V. Ebsworth, S. G. Frankiss, and A. G. Robiette, J. Mol. Spectroscopy, 1964, 12, 299.

<sup>15</sup> J. E. Drake and W. L. Jolly, J. Chem. Soc., 1962, 2807.

each satellite peak appearing as a 1:3:3:1 quartet. The ratio of higher silanes to selenium-containing product species was *ca.* 1:1.

The mass spectrum gave parent peaks at m/e 64 (Si<sub>2</sub>H<sub>6</sub>), 95 (Si<sub>3</sub>H<sub>8</sub>), 113 (SiH<sub>3</sub>SeH), and 126 (Si<sub>4</sub>H<sub>10</sub>).

 $GeH_4/H_2S$ . The products from a series of 1 h discharges gave resonances in the <sup>1</sup>H n.m.r. spectrum at 3.24 (Ge<sub>2</sub>H<sub>6</sub>),<sup>14</sup> 3.3 (Ge<sub>3</sub>H<sub>8</sub>), 3.3 and 3.4 (iso- and n-Ge<sub>4</sub>H<sub>10</sub>),  $^{15}$  4.50 and -0.29 (GeH<sub>3</sub>SH), and 4.64 p.p.m. [(GeH<sub>3</sub>)<sub>2</sub>S].<sup>13,16</sup> The ratio of higher germanes to sulphur-containing product species was ca. 4: 1.

 $GeH_4/H_2Se$ . The products from a series of 1 h discharges gave resonances in the <sup>1</sup>H n.m.r. spectrum at 4.15 and -2.38 p.p.m. (GeH<sub>3</sub>SeH), and 4.29 p.p.m. [(GeH<sub>3</sub>)<sub>2</sub>Se],<sup>13,17</sup> as well as those attributable to  $\text{Ge}_2\text{H}_6$ <sup>14</sup> and  $\text{Ge}_3\text{H}_8$ .<sup>15</sup> The ratio of higher germanes to selenium-containing product species was ca. 5: 1.

 $SiH_4/GeH_4/H_2S$ . In addition to the products observed from the discharges on SiH<sub>4</sub>/H<sub>2</sub>S and GeH<sub>4</sub>/H<sub>2</sub>S mixtures, the <sup>1</sup>H n.m.r. spectrum contained a complex feature at 3.0-3.5 p.p.m. attributable to silylgermanes 18 and two related 1:3:3:1 quartets,  $(|J_{HH'}| 0.80$  Hz), of equal intensity at 4.40 and 4.64 p.p.m. (SiH\_3SGeH\_3').19 The ratio of higher and mixed Group IV hydrides to sulphurcontaining product species was ca. 2:1.

The following silylgermanes were identified by mass spectroscopy:  $SiH_3GeH_3$  (m/e 111),  $Si_2GeH_8$  (m/e 142),  $SiGe_2H_8$  (m/e 189), and trace amounts of  $Si_xGe_{4-x}$ . Parent peaks for the other Group IV hydride products were observed at m/e 158 (Ge<sub>2</sub>H<sub>6</sub>), 236 (Ge<sub>3</sub>H<sub>8</sub>), 64 (Si<sub>2</sub>H<sub>6</sub>), 95 (Si<sub>3</sub>H<sub>8</sub>), and 126 (Si<sub>4</sub>H<sub>10</sub>).

SiH<sub>4</sub>/GeH<sub>4</sub>/H<sub>2</sub>Se. In addition to the products observed from the discharges on SiH<sub>4</sub>/H<sub>2</sub>Se and GeH<sub>4</sub>/H<sub>2</sub>Se mixtures, the <sup>1</sup>H n.m.r. spectrum contained a complex feature at  $3 \cdot 0 - 3 \cdot 5$  p.p.m. (silylgermanes) <sup>18</sup> and two related 1 : 3 : 3 : 1quartets,  $(|J_{\rm HH'}| 0.73 \text{ Hz})$ , of equal intensity at 4.15 and 4.25 p.p.m. (SiH<sub>3</sub>SeGeH<sub>3</sub>').<sup>19</sup> The ratio of higher and mixed Group IV hydrides to selenium-containing product species was ca. 3: 1.

The mass spectrum gave parent peaks for the Group IV hydrides  $Ge_2H_6$ ,  $Ge_3H_8$ ,  $Si_2H_6$ ,  $Si_3H_8$ ,  $Si_4H_{10}$ ,  $SiGeH_6$ , Si<sub>2</sub>GeH<sub>8</sub>, and Si<sub>2</sub>Ge<sub>2</sub>H<sub>8</sub>.

MeSH. The major product of the discharge of MeSH was shown by <sup>1</sup>H n.m.r. analysis to be Me<sub>2</sub>S<sub>2</sub> containing some Me<sub>2</sub>S (singlets at 2.27 and 2.01 p.p.m. respectively <sup>20</sup>). The mass spectrum gave peaks at m/e 94 (Me<sub>2</sub>S<sub>2</sub>), 79  $(MeS_2)$ , 64  $(S_2)$ , 47 (MeS) attributable to  $Me_2S_2$ , and at m/e 62, attributable to Me<sub>2</sub>S.

 $SiH_4/MeSH$ . The products from a series of 1 h discharges were analysed in the <sup>1</sup>H n.m.r. which showed related quartets ( $|J_{\rm HH'}|$  0.45 Hz) of equal intensity at 2.08 and 4.30 p.p.m. attributable to MeSSiH<sub>3</sub>',<sup>21</sup> and peaks attributable to  $Me_2S$ ,  $Me_2S_2$ ,<sup>20</sup> the higher silanes,<sup>11,12</sup> and (SiH<sub>3</sub>)<sub>2</sub>S.<sup>13</sup> The ratio of higher silanes to sulphur-containing silicon products was ca. 1:5.

The mass spectrum gave parent peaks at m/e 62 (Me<sub>2</sub>S),

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64 (Si\_2H\_6), 79 (MeSSiH\_3), 94 (Me\_2S\_2), 96 [(SiH\_3)\_2S], and 126 (Si\_4H\_{10}).

GeH<sub>4</sub>/MeSH. The <sup>1</sup>H n.m.r. spectra of the products from a series of 1 h discharges were analysed and showed related quartets, ( $|J_{HH'}| 0.60 \text{ Hz}$ ), of equal intensity at 2.15 and 4.65 p.p.m. attributable to MeSGeH<sub>3</sub>',<sup>22</sup> and peaks attributable to Me<sub>2</sub>S, Me<sub>2</sub>S<sub>2</sub>,<sup>20</sup> higher germanes,<sup>14,15</sup> and (GeH<sub>3</sub>)<sub>2</sub>S.<sup>13,16</sup> The ratio of higher germanes to sulphurcontaining germanium products was ca. 1: 2.

 $|J_{\rm HH'}|$  values of related hydrides (Hz)

MeSCH <sub>3</sub> '	0.30 a	SiH <sub>s</sub> SCH <sub>s</sub> '	0·45 <sup>b</sup>
MeSSiH <sub>3</sub> '	0.45 b	SiH <sub>s</sub> SSiH <sub>s</sub> '	0·70 c
MeSGeH <sub>3</sub> '	0.60 d	SiH <sub>s</sub> SGeH <sub>s</sub> '	0·80
MeSeCH <sub>3</sub> '	0.15 e	SiH <sub>s</sub> SeGeH <sub>s</sub> '	0·73
MeSeCH <sub>3</sub> ' SiH <sub>3</sub> SeSiH <sub>3</sub> '	0.15 ° 0.63	SiH <sub>3</sub> SeGeH <sub>3</sub> '	0.73

 ${\rm GeH_3SGeH_3'}$  and  ${\rm GeH_3SeGeH_3'}$  not observed

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## DISCUSSION

When silane and germane react with hydrogen sulphide, hydrogen selenide, and methanethiol under the stimulation of a high-voltage ozoniser-type silent electric discharge, considerable breakdown occurs although not to the same extent as in Group IV-Group V hydride mixtures under analogous conditions (ca. 10% compared with ca. 25% after 1 h).<sup>3,23</sup>

Mixed hydride species are formed, viz.  $MH_3EH$  and  $(MH_3)_2E$  from  $MH_4/H_2E$  mixtures (M = Si or Ge; E = S or Se), as well as higher binary hydrides,  $M_nH_{2n+2}$  (n = 2-4) in amounts detectable by <sup>1</sup>H n.m.r. spectroscopy. Reaction mechanisms in these types of discharges are not well understood. However, the product distribution indicates that the breaking of an M-H bond may be the most important initial step. Subsequent reactions (1) and (2) would then account for the con-

$$\cdot MH_3 + H_2E \longrightarrow MH_3EH + H \cdot$$
 (1)  
 
$$\cdot MH_3 + MH_4 \longrightarrow MH_3MH_3 + H \cdot$$
 (2)

siderable amounts of  $MH_3EH$  and  $M_2H_6$  observed. Similarly, the low yield of  $H_2E_2$  is rationalised. (Alternatively, M-H cleavage could give  $MH_2$  followed by insertion into  $H_2E$  or  $MH_4$ .) The formation of the higher binary hydrides results from reaction of  $\cdot MH_3$ with  $M_2H_6$  etc., but it is probable that  $(MH_3)_2E$  species are not principally direct discharge products. The equilibrium reactions (3) are well known and as soon as

$$2\mathrm{MH}_{3}\mathrm{EH} \Longrightarrow (\mathrm{MH}_{3})_{2}\mathrm{E} + \mathrm{H}_{2}\mathrm{E} \qquad (3)$$

 $MH_3EH$  is formed this equilibrium will be established. Similarly, in the systems,  $SiH_4/GeH_4/H_2E$ , the formation of the 'quarternary' species,  $SiH_3EGeH_3$  results mainly from condensation of  $SiH_3EH$  and  $GeH_3EH$  reaction (4).

$$SiH_3EH + GeH_3EH \implies SiH_3EGeH_3 + H_2E$$
 (4)

Thus the <sup>1</sup>H n.m.r. spectrum initially shows strong signals for SiH<sub>3</sub>EH and GeH<sub>3</sub>EH. Sequential recording of the spectrum however, indicates that these signals decrease in intensity as those due to  $(SiH_3)_2E$ ,  $(GeH_3)_2E$ , and SiH<sub>3</sub>EGeH<sub>3</sub> increase.

In the  $MH_4/MeSH$  reactions, the principal process involves the breaking of the S-H bond, because the decomposition of the  $MH_4$  species is considerably quenched and when MeSH is discharged alone, considerable amounts of  $Me_2S_2$  are formed, reaction (5).

$$MeS \cdot + MeSH \longrightarrow Me_2S_2 + H \cdot$$
 (5)

There is a high yield of  $MeSMH_3$  as expected for reaction (6), while  $MeMH_3$  and  $M_2H_6$  species are produced

$$MeS' + MH_4 \longrightarrow MeSMH_3 + H'$$
(6)

in low yield.

The long-range coupling constant, J [H-(M-E-M'-)H], has now been observed in all the known MH<sub>3</sub>EM'H<sub>3</sub> species (M = C, Si, or Ge; M' = C or Si; E = S or Se). Its absolute value is observed to increase in the series MH<sub>3</sub>-EM'H<sub>3</sub> for different M in the order C < Si < Ge (Table).<sup>19,22</sup> No value has been obtained from the digermyl compounds, (GeH<sub>3</sub>)<sub>2</sub>E, as germanium lacks a suitable isotope to exhibit such coupling in a satellite spectrum. Long-range coupling is not observed for E=O and it is suggested that the *d* orbitals of sulphur and selenium allow the transmission of the coupling, a mechanism unavailable to oxygen.

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