

RELATIVE RATES OF GERMYLENE AND SILYLENE INSERTIONS INTO ALKYLGERMANES IN COMPETITION WITH DIGERMANE AND DI-SILANE

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SUMMARY

The relative rates of GeH_2 insertions into the Ge-H bonds on a per bond basis were found to be in the order: $(\text{CH}_3)_3\text{GeH} > (\text{CH}_3)_2\text{GeH}_2 > \text{Ge}_2\text{H}_6 > \text{CH}_3\text{GeH}_3$. These results were determined from competitive reactions of GeH_2 with Ge_2H_6 and alkylgermanes. The relative rates of SiH_2 insertions into Si_2H_6 versus $(\text{CH}_3)_2\text{GeH}_2$ and $(\text{CH}_3)_3\text{GeH}$ were also obtained.

These relative rates and those previously reported were examined for a correlation with the bond energy of the bond undergoing insertion and with the negative charge of the hydrogen in the bond undergoing insertion. The correlation with bond energies was successful for germanes or silanes considered separately but not for SiH_2 insertions into CH_3SiH_3 , CH_3GeH_3 and CH_3PH_2 . The correlation with the negative charge on the hydrogen was unsuccessful only where steric factors could be important.

INTRODUCTION

The chemistry of the germanium analogs of methylene has generally been limited to the germanium dihalides. Reactions of germylene (GeH_2) have been reported from recoiling germanium atoms¹ and from the pyrolysis of Ge_2H_6 ². Although GeH_2 insertion into Ge-H bonds has been demonstrated^{1,2}, little is known concerning its chemistry. In connection with a recent investigation of silylene insertion reactions³, a study of relative germylene insertion rates was undertaken by examining competitive insertions of GeH_2 into Ge_2H_6 and other hydrides. In this paper, we report the results of that study and present some generalizations concerning the chemistry of SiH_2 and GeH_2 .

RESULTS

Digermane has been shown to decompose by a 1,2-hydrogen shift to produce GeH_4 and GeH_2 (Eq. 1)². The reactive intermediate, GeH_2 , can insert into Ge_2H_6 to form Ge_3H_8 (Eq. 2) or polymerize on the wall².



Since the trigermene insertion product is slightly less stable than digermene, the insertion reactions were carried out in a recirculating flow system containing a low temperature trap which removed the less volatile (and often less stable) products from the stream. All of the trapping agents used were stable at the reaction temperature (except digermene).

A. Insertion reactions of GeH_2

The results listed in Table 1 were obtained from the flow pyrolysis of digermene at 280° in the presence of a second GeH_2 trapping agent. The relative insertion rates of germylene into the methylgermanes and trimethylsilane can best be compared on a per-bond basis.

The results listed in Table 1 are valid provided that the insertion products did not decompose before they were removed from the reaction stream by the cold trap. Control reactions with deuterated trapping agents demonstrated that secondary reactions did not occur in our system.

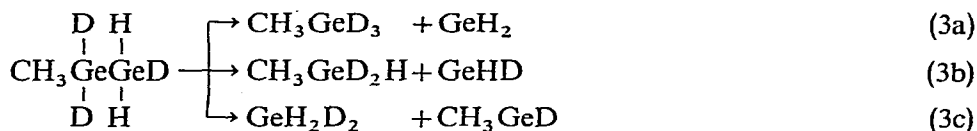
TABLE 1

RELATIVE INSERTION RATE OF GeH_2 AT 280°C (per E-H bond, E=Si or Ge)

Experiment	Trapping agent	Insertion product	Relative insertion rate
1	Ge_2H_6	Ge_3H_8	1.0
2	$(\text{CH}_3)_3\text{GeH}$	$1,1,1-(\text{CH}_3)_3\text{Ge}_2\text{H}_3$	1.8 ± 0.2
3	$(\text{CH}_3)_2\text{GeH}_2$	$1,1-(\text{CH}_3)_2\text{Ge}_2\text{H}_4$	1.3 ± 0.15
4	CH_3GeH_3	$\text{CH}_3\text{Ge}_2\text{H}_5$	0.8 ± 0.1
5	$(\text{CH}_3)_3\text{SiH}$	$(\text{CH}_3)_3\text{SiGeH}_3^a$	$< 0.01^a$

^a Insertion product not observed.

The pyrolysis of Ge_2H_6 in the presence of CH_3GeD_3 produced methyl-digermene- d_3 (presumably $\text{CH}_3\text{GeD}_2\text{GeH}_2\text{D}$). This methyl-digermene is expected to decompose via a 1,2-hydrogen shift (similar to Ge_2H_6) and produce among other products GeH_2D_2 (Eq. 3a-3c). The methyl-digermene- d_3 -trigermene fraction obtained



from our control reaction was pyrolysed at 295° for 15 minutes and the volatile products included GeH_2D_2 as expected.

The absence of GeH_2D_2 from the 280° pyrolysis of Ge_2H_6 with CH_3GeD_3 demonstrates that methyl-digermene was quantitatively removed in our system. Since the methylated digermanes are of similar stabilities and slightly more stable than digermene⁴, these results imply that $1,1-(\text{CH}_3)_2\text{Ge}_2\text{H}_4$ and $1,1,1-(\text{CH}_3)_3\text{Ge}_2\text{H}_3$ were

also quantitatively removed in our flow system. If GeH_2 did insert into $(\text{CH}_3)_3\text{SiD}$ to form $(\text{CH}_3)_3\text{SiGeH}_2\text{D}$, and if this compound decomposed prior to condensation in the low temperature trap, $(\text{CH}_3)_3\text{SiH}$ would probably be a product since SiH_3GeH_3 decomposes solely to SiH_4 ⁵. The absence of $(\text{CH}_3)_3\text{SiH}$ in our control experiment suggests that GeH_2 did not insert into $(\text{CH}_3)_3\text{SiH}$.

Although a control reaction to verify the complete removal of Ge_3H_8 could not be performed (due to the difficulty in preparing large quantities of Ge_2D_6 and the lack of data on the modes of trigermane decomposition), arguments will be presented to support this contention. Trisilane was shown to be quantitatively removed in the pyrolysis of Si_2H_6 ³. Trigermane was found only slightly less stable than Ge_2H_6 when mixtures were co-pyrolysed, while Si_3H_8 is considerably less stable than Si_2H_6 . In addition, there is a larger difference in volatility between di- and trigermane than there is between di- and trisilane. Thus, both factors which determine the effectiveness of product removal (high thermal stability and low volatility) are favored for Ge_3H_8 and therefore it should have been removed as well as Si_3H_8 was in the Si_2H_6 pyrolysis. It is well to note that even if some Ge_3H_8 had decomposed, its effects would be similar in each of the experiments (exp. 2-5) and the results would not lose their significance in a relative sense.

The pyrolysis of Ge_2H_6 was also carried out in the presence of CH_3SiH_3 without the formation of $\text{CH}_3\text{SiH}_2\text{GeH}_3$. However, it appears that $\text{CH}_3\text{SiH}_2\text{GeH}_3$ is more volatile than Ge_2H_6 ⁵ and it may not have been retained in our cold trap. Data from the pyrolysis of GeH_3SiH_3 in the presence of CH_3SiH_3 suggest that GeH_2 insertion into the Si-H bond in CH_3SiH_3 does occur but with a rate an order of magnitude slower than into the Ge-H bond in GeH_3SiH_3 ⁵. Results from recoiling germanium atoms in the presence of GeH_4 and SiH_4 suggest that the relative insertion rate¹ of GeH_2 into GeH_4 and SiH_4 is about 4/1.

B. Insertion reactions of SiH_2

Table 2 consists of new data on silylene insertions into the methylgermanes

TABLE 2

RELATIVE INSERTION RATE OF SiH_2 AT 350°C (per E-H bond, E=Si or Ge)

Experiment	Trapping agent	Insertion product	Relative insertion rate	Ref.
1	Si_2H_6	Si_3H_8	1.0	^a
2	$(\text{CH}_3)_3\text{SiH}$	1,1,1- $(\text{CH}_3)_3\text{Si}_2\text{H}_3$	1.6 ± 0.2	^a
3	$(\text{CH}_3)_2\text{SiH}_2$	1,1- $(\text{CH}_3)_2\text{Si}_2\text{H}_4$	0.7 ± 0.1	^a
4	CH_3SiH_3	$\text{CH}_3\text{Si}_2\text{H}_5$	0.4 ± 0.05	^a
5	SiH_4	Si_2H_6	0.3 ± 0.1	^b
6	ClSiH_3	$\text{ClSi}_2\text{H}_5^d$	$< 0.01^d$	^a
7	$(\text{CH}_3)_3\text{GeH}$	1,1,1- $(\text{CH}_3)_3\text{GeSiH}_3$	4 ± 2^c	^c
8	$(\text{CH}_3)_2\text{GeH}_2$	1,1- $(\text{CH}_3)_2\text{GeHSiH}_3$	6.4 ± 0.5	^c
9	CH_3GeH_3	$\text{CH}_3\text{GeH}_2\text{SiH}_3$	0.2 ± 0.05 0.02	^a
10	CH_3PH_2	$\text{CH}_3\text{PHSiH}_3^d$	$< 0.01^d$	^a

^a Ref. 3. ^b Ref. 21. ^c This work. ^d Insertion product not observed. ^e See experimental section.

as well as previously reported insertion rates included for ease of comparison. The control experiments required are described in our earlier paper³ which demonstrated the Si_3H_8 was quantitatively removed by the cold trap and that $\text{CH}_3\text{GeH}_2\text{SiH}_3$ was almost quantitatively removed from the stream. Di- and trimethylgermane are stable at 350°.

DISCUSSION

The relative rates of GeH_2 insertion into Ge-H bonds in monogermanes (exps 2-4 in Table 1) and of SiH_2 insertion into Si-H bonds in monosilanes (exps 2-6 in Table 2) correlate well with the Ge-H or Si-H stretching frequencies. For silicon and germanium, these stretching frequencies decrease as methyl groups replace hydrogen atoms and increase as chlorine replaces hydrogen. As the frequency decreases, the insertion rate increases. The stretching frequencies can be related to both the charge on the hydrogen atom and the bond strength. A decrease in stretching frequency corresponds to decrease in bond strength. This corresponds to an increase in the "p" character of the germanium or silicon orbital bonded to hydrogen which also corresponds to an increase in the negative charge on the hydrogen^{7,8}. The increased rates of insertion for GeH_2 into Ge-H bonds and SiH_2 into Si-H bonds can thus be correlated with either a decrease in E-H bond strength (E=Si or Ge) or an increase in the negative charge on the H atom undergoing insertion.

The low insertion rate for GeH_2 into $(\text{CH}_3)_3\text{SiH}$ in competition with Ge_2H_6 (exps 1 and 5 in Table 1) and the high insertion rates of SiH_2 into $(\text{CH}_3)_2\text{GeH}_2$ and $(\text{CH}_3)_3\text{GeH}$ in competition with Si_2H_6 (exps 1, 7 and 8 in Table 2) could be explained on the basis of bond energies. That is, the insertion rate is faster into the weaker bond. This rationalization would also explain the relative rates of $^3\text{HCCl}$ insertion into the Si-H bonds⁹ in $(\text{CH}_3)_3\text{SiH}$, $(\text{CH}_3)_2\text{SiH}_2$ and SiH_4 which were determined to be $6/1 < 0.1$. Similarly the insertion of $^1\text{CH}_2$ into CH_3SiH_3 is favored into the Si-H bonds versus the C-H bonds by a factor¹⁰ of 8.9 while CCl_2 insertion into $(\text{C}_2\text{H}_5)_3\text{GeH}$ was found to be 4.5 times greater than into $(\text{C}_2\text{H}_5)_3\text{SiH}$ ¹¹.

However, the regulation of relative insertion rates by bond energies does not appear to explain the results of the relative insertion rates of SiH_2 into CH_3SiH_3 versus insertion into CH_3GeH_3 or CH_3PH_2 . The Si-H bond energy is greater than that of the Ge-H bond¹² while the Si-H and P-H bond energies are very similar¹². Thus the relative insertion rates of SiH_2 into CH_3SiH_3 , CH_3GeH_3 and CH_3PH_2 should be in the order, $\text{CH}_3\text{GeH}_3 > \text{CH}_3\text{SiH}_3 \cong \text{CH}_3\text{PH}_2$, and not in the observed order of $\text{CH}_3\text{SiH}_3 > \text{CH}_3\text{GeH}_3 \gg \text{CH}_3\text{PH}_2$. The observed order correlates exactly with the charge on the hydrogen; the greater the negative charge on the hydrogen, the faster the insertion. This rationalization would also be consistent with the HCCl insertions into silanes and that of CH_2 into CH_3SiH_3 . It is interesting to note that the correlation between insertion rates and the negative charge on hydrogen only breaks down in cases where steric factors could be important. The low rate of GeH_2 insertion into $(\text{CH}_3)_3\text{SiH}$ versus $(\text{CH}_3)_3\text{GeH}$ and the high rate of SiH_2 insertion into $(\text{CH}_3)_3\text{GeH}$ and $(\text{CH}_3)_2\text{GeH}_2$ versus $(\text{CH}_3)_3\text{SiH}$ and $(\text{CH}_3)_2\text{SiH}_2$ respectively could be due to or at least affected by steric factors. Similarly, the greater rate of CCl_2 insertion into $(\text{C}_2\text{H}_5)_3\text{GeH}$ versus $(\text{C}_2\text{H}_5)_3\text{SiH}$ could also be due to steric factors.

EXPERIMENTAL

Reagents. Disilane, methylsilanes, methylgermane, and trimethylgermane were prepared by the reduction of the corresponding chlorides with LiAlH_4 or LiAlD_4 . Dimethylgermane was prepared from methylgermane as described by Jolly¹³. Digermane was prepared from the static pyrolysis of GeH_4 at 340° (350 mm) for intervals of 1–2 min. Germane was obtained from the NaBH_4 reduction of GeO_2 ¹⁴. These reagents were purified by trap to trap distillations and were identified by infrared and mass spectra. The purity of these compounds was demonstrated by GLPC as well as by demonstrating that infrared bands and mass spectral peaks of logical impurities were absent from the spectra of these compounds.

Instrumental. Infrared spectra were recorded on a Perkin–Elmer 337 or 621 spectrophotometer while mass spectra were obtained on a Hitachi–Perkin–Elmer RMU-6E spectrometer. The product hydrides were separated by GLPC as previously described³.

General procedure. The pyrolyses were carried out in a recirculating flow system consisting of a Toepler pump, thermal zone and “U”-trap. The thermal zone was a 10 cm \times 10 mm O.D. pyrex tube heated by means of a high temperature tape and insulated with magnesia insulation. Temperatures were measured by means of a thermometer inserted in a pyrex well between the heating tape and the thermal zone. The temperature was regulated by a constant voltage power supply. The pyrex thermal zone was coated with a silicon mirror from silane decompositions for the Si_2H_6 pyrolyses and coated with a germanium mirror for Ge_2H_6 pyrolyses to avoid pyrex catalysis.

Analysis. Authentic samples of the reaction products were obtained from the pyrolysis of digermane or disilane with the appropriate trapping agent as indicated in Tables 1 and 2. The infrared spectra of Ge_3H_8 ¹⁵, $\text{CH}_3\text{Ge}_2\text{H}_5$ ¹⁶, $1,1\text{-(CH}_3)_2\text{Ge}_2\text{H}_4$ ¹⁷, $1,1,1\text{-(CH}_3)_3\text{Ge}_2\text{H}_3$ ¹⁸, and $1,1,1\text{-(CH}_3)_3\text{GeSiH}_3$ ¹⁹ were identical to those in the literature. The mass spectra of these compounds were consistent with their formulae. The previously unreported compound $1,1\text{-(CH}_3)_2\text{GeHSiH}_3$ is described below. Authentic product and reagent samples were used to determine GLPC retention times and weight correction factors.

A1. Competitive reactions with Ge_2H_6 at 280°C

The data in Table 3 represent the average of at least three identical reactions for each system. The pyrolysis cold traps listed in Table 3 were used during the pyrolyses. After each reaction, the mixture was fractionated and the product was condensed in the condensation cold trap as listed in Table 3.

A2. Control reactions with Ge_2H_6

CH_3GeD_3 . Methylgermane- d_3 and digermane (0.92 mmol each) were pyrolysed at 295° for 6 h with a -63° cold bath. The germane fraction (pass -160° , stop -196° ; 0.33 mmol) was analyzed by infrared and mass spectrometry for the presence of deuterated germanes. The infrared spectrum was primarily that of GeH_4 with very weak absorptions at 706 and 901 cm^{-1} due to GeH_3D ²⁰. Some GeD_3H (595, 625 and 790 cm^{-1})²⁰ may also have been present. Absorptions due to GeH_2D_2 (657, 770 and 880 cm^{-1})²⁰ were absent. Mass spectral results are tabulated below. The fraction

TABLE 3

PYROLYSES OF Ge_2H_6 AT 280°C

Reagent (mmol)	Ge_2H_6 (mmol)	Pyrolysis cold trap ($^\circ\text{C}$)	Gas phase ratio reagent/ Ge_2H_6	Condensation cold trap ($^\circ\text{C}$)	Product ratio
1 $(\text{CH}_3)_3\text{GeH}$ (0.95)	0.49	-63	1.64	-95	$\frac{1,1,1-(\text{CH}_3)_3\text{Ge}_2\text{H}_3}{\text{Ge}_3\text{H}_8} = 0.50$
2 $(\text{CH}_3)_2\text{GeH}_2$ (0.48)	0.48	-63	3.56	-112	$\frac{1,1-(\text{CH}_3)_2\text{Ge}_2\text{H}_4}{\text{Ge}_3\text{H}_8} = 1.54$
3 CH_3GeH_3 (0.98)	0.98	-63	5.88	-112	$\frac{\text{CH}_3\text{Ge}_2\text{H}_5}{\text{Ge}_3\text{H}_8} = 2.44$
4 $(\text{CH}_3)_3\text{SiH}$	0.85	-78	~2	-95	Ge_3H_8 only

TABLE 4

PARTIAL MASS SPECTRA OF THE GERMANE FRACTION AFTER PYROLYSIS

<i>m/e</i>	76	77	78	79	80	81
Pure GeH_4	1000	805	165	165	0	0
Pass -160° fraction from Ge_2H_6 - CH_3GeD_3	1000	785	230	160	22	0
Pass -160° fraction from product pyrolysis	1000	810	400	200	65	35

which passed -78° and stopped at -95° was pyrolyzed for 15 minutes at 295° without a cold bath. The germane fraction from this second pyrolysis was too small for infrared analysis, but the mass spectrum (Table 4) indicated the presence of GeH_2D_2 from the decomposition of the GeH_2 insertion product (presumably $\text{CH}_3\text{GeD}_2\text{GeH}_2\text{D}$).

$(\text{CH}_3)_3\text{SiD}$. Trimethylsilane- d_1 and Ge_2H_6 were pyrolyzed as shown in exp. 4, Table 3. The infrared spectra of all fractions obtained did not contain absorptions due to Ge-D bonds (approx. 1500 cm^{-1}) or to Si-H bonds (approx. 2120 cm^{-1}).

B1. Competitive reactions with Si_2H_6 at 350°

The following data represent average results of at least three identical reactions.

$(\text{CH}_3)_3\text{GeH}$. A mixture of 1.47 mmol of $(\text{CH}_3)_3\text{GeH}$ and 0.30 mmol of Si_2H_6 were pyrolyzed for 6 h with a -78° bath. The gas phase ratio $\text{Si}_2\text{H}_6/(\text{CH}_3)_3\text{GeH}$ was 1.6. The small quantities and very large retention time of $(\text{CH}_3)_3\text{GeSiH}_3$ precluded determination of the GLPC weight correction factor and accurate measurement of peak areas. The stop -112° fraction consisted of a 2.5 ± 1 excess of Si_3H_8 over $(\text{CH}_3)_3\text{GeSiH}_3$.

$(\text{CH}_3)_2\text{GeH}_2$. Dimethylgermane (0.58 mmol) and disilane (0.48 mmol) were pyrolyzed with a -78° trapping bath which set the gas phase ratio at 0.34. After 6 h, the stop -112° fraction contained $(\text{CH}_3)_2\text{GeHSiH}_3/\text{Si}_3\text{H}_8$ (=0.71).

B2. Identification of $(\text{CH}_3)_2\text{GeHSiH}_3$

The dimethylgermylsilane prepared in exp. 8 (Table 2) was identified as follows: (i) The gas phase infrared spectrum consists of the following absorptions: 2975 m, 2920 m, 2146 vs, 2029 s, 1381 w, 1250 w, 922 m, 878 s, 828 vs, 705 m, 669 m, 585 m cm^{-1} . (ii) The mass spectrum consisted of peaks due to the heavy atom skeletons (envelope intensity); C_2GeSi^+ (20.8), CGeSi^+ (47), GeSi^+ and C_2Ge^+ (100), CGe^+ (61.7), Ge^+ (18.3). At higher voltages CSi^+ fragments were observed due to methyl migration as reported for $(\text{CH}_3)_3\text{GeSiH}_3$ by Mackay *et al.*¹⁷.

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