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REACTIONS OF TRIMETHYLGALLIUM WITH SILICON HYDRIDES, GERMANE AND DIBORANE

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Summary

Methylation of SiH_4, $MeSiH_3$, Si_2H_6, GeH_4 and B_2H_6, but not of PH_3 or AsH_3, was observed during reaction (230—324°C) with $GaMe_3$. The products from the SiH_4 and Si_2H_6 reactions were $MeSiH_3$, Me_2SiH_2 and Me_3SiH. The GeH_4-derived products were similar, with Me_4Ge also being formed. The only methylated products from B_2H_6 was BMe_3. The silane reactions were surface-catalyzed (presumably by surface hydroxyl groups), while those of GeH_4 and B_2H_6 may have occurred via gas-phase free radical processes.

Introduction

The formation of $2\text{-}CH_3B_5H_8$ from the thermal reaction of BMe_3 with B_5H_9 has been reported recently [1]. Trimethylgallium was found to be a catalyst for this reaction [1]. In addition, when $GaMe_3$ was present during the BMe_3/B_5H_9 reaction, the BMe_3 recovery was 120%, suggesting that $GaMe_3$ reacted with B_5H_9 to form BMe_3. We report results of an investigation of $GaMe_3$ reactions with B_2H_6, GeH_4 and silicon hydrides which were suggested by the above observation.

Experimental

Separations and transfers were carried out in Pyrex glass vacuum systems which operated at 10^{-4}—10^{-5} mmHg. The silanes [2], GeH_4 [3], AsH_3 [3], PH_3 [4] and B_2H_6 [5] were prepared as described in the literature. The $GaMe_3$ was obtained from the Ventron Corporation or prepared by reaction of Al_2Me_6 with $GaCl_3$.

The reactions with $GaMe_3$ were carried out in cylindrical Pyrex vessels, 25 cm in length with a diameter of 35 mm, which were fitted with Teflon valves and standard taper joints for attachment to the vacuum systems. The vessels were heated by heating tapes which were well insulated with asbestos. Temperatures were measured by a thermocouple inserted into a well in the bottom of the reaction vessel. For some reactions, the lower 15 cm of the reaction vessel was packed with Pyrex beads. The geometrical surface areas were about 0.019 sq. meters and 0.187 sq. meters for the unpacked and packed reactors, respectively.

The surfaces were cleaned with NaOCl (5% soln), 16 *M* HNO_3 and then rinsed with distilled H_2O. The reaction vessels were then heated at 230°C for 18 h under dynamic vacuum prior to each experiment. For the GeH_4 experiments, a solution of 2 parts HF/9 parts HNO_3 was used to remove the germanium films.

Infrared spectra were obtained on a Perkin—Elmer model 337 spectrometer in 10 cm gas cells fitted with KBr windows. Mass spectra were obtained with a Perkin—Elmer RMU-6E spectrometer at 10 or 70 eV. Gas chromatographic determinations were made on a Carle Model 8004 chromatograph using a 24 ft, 20% squalene, column.

Product identifications were made as follows. The SiH_4/Me_3Ga reaction mixture was distilled from the reaction vessel and Toepler pumped through traps cooled to —196°C into a calibrated volume for quantitative measurement of the H_2/CH_4 product mixture. The relative ratio of this mixture was determined mass spectroscopically with the use of a standard mixture. The fraction condensed at —196°C then was partially separated by trap-to-trap distillations. The fraction passing a —160°C trap was SiH_4, identified by an infrared spectrum. The fraction condensed at —78°C was $GaMe_3$, identified by an infrared spectrum which did not contain an Si—H stretching band (2200—2100 cm^{-1}) or absorptions of $SiMe_4$ (1240, 860 or 690 cm^{-1}). The fraction passing —78°C and condensed at —160°C was a mixture of $MeSiH_3$, Me_2SiH_2 and Me_3SiH. The infrared and mass spectra of these mixtures consisted of the superposition of those for $MeSiH_3$, Me_2SiH_2 and Me_3SiH. The GLC retention times were those of authentic samples of the methylsilanes. The absence of Si_2H_6 was demonstrated by the nonexistence of the very strong IR absorption at 830 cm^{-1}. Similar identifications were made for the $MeSiH_3/Me_3Ga$ reaction mixtures. For the Si_2H_6 reaction, the quantitative analysis for Me_2SiH_2 was made mass spectrometrically with standardized spectra obtained on our spectrometer. The germanes and BMe_3 were identified in the same manner with infrared and mass spectra. Germane analyses were obtained by GLC while BMe_3 was isolated as the pure material.

Results and discussion

The reaction of $GaMe_3$ with various hydrides has been examined neat in Pyrex reaction vessels with and without Pyrex beads. The beads increased the surface area by a factor of ten, while the volume was decreased by a factor of about two. Typical results for reactions in the packed vessels are listed in Table 1, while those in the unpacked vessels are listed in Table 2.

In Table 1, the experiments listed are those which were carried out over a surface which had been used previously for the same reaction but cleaned as described in the experimental section. The experiments listed in Table 2 (without beads) were carried out in the following manner. A new reaction vessel

TABLE 1

REACTIONS OF $GaMe_3$ IN A PACKED REACTION VESSEL

	Temp. (°C)	Time (min)	Reagents added (mmol)		Products and unused reagents (mmol)						
			hydride	Me_3Ga	hydride	Me_3Ga	H_2	CH_4	$MeEH_3$ ($E = Si, Ge$)	Me_2EH_2	Me_3EH
SiH_4 [a]	310	120	0.46	0.41	0.34	0.29	0.08	0.12	0.01	0.06	0.03
SiH_4 [b]	296	60	0.20	0.11	0.18	0.02	0.01	0.03	0.003	0.004	0.004
$MeSiH_3$ [b]	270	40	0.16	0.18	0.11	0	0.05	0.18	—	0.04	0.001
Si_2H_6 [b,c]	262	90	0.27	0.32	0	0	0.08	0.14	0.13	0.05	0.02
GeH_4 [a,d]	302	120	0.92	0.91	0.38	0.24	0.59	0.31	0.005	0.003	0.49
B_2H_6 [a]	230	180	0.83	0.92	0	0.14	2.01	0.14	BMe_3	(0.62)	

[a] Reagents condensed into reaction vessel at −196°C. [b] Reagents expanded into heated reaction vessel. [c] No SiH_4 or $MeSi_2H_5$ observed. [d] Tetramethylgermane (0.02 mmol) also prepared.

TABLE 2

REACTIONS OF SiH_4 WITH $GaMe_3$ [a] (unpacked)

	Temp. (°C)	Time (min)	Reagents (mmol)		Products and unused reagents							
			SiH_4	Me_3Ga	SiH_4	Me_3Ga	H_2	CH_4	C_2H_6	$MeSiH_3$	Me_2SiH_2	Me_3SiH
1	324	30	0.20	0.17	0.20	0.17	—	—	—	—	—	—
2	338	1050	0.18	0.23	—	0.02	0.09	0.31	—	—	0.05	0.08
3	320	65	0.18	0.21	0.12	0.16	0.02	0.04	—	0.005	0.03	0.02
4	324	60	0.14	0.25	0.12	0.17	0.01	0.03	0.002	0.002	0.01	0.004
5	322	60	0.26	0.16	0.22	0.06	0.03	0.05	0.01	0.006	0.01	0.003

[a] Reagents expanded into the heated reaction vessel.

(untouched by chemicals) was used for reaction 1. Reaction 2 and 3 were carried out in the vessel from reaction 1 over the surface from the previous experiment. The vessel was cleaned as described in the experimental section and reaction 4 was carried out. Reaction 1 was repeated in a new vessel. The surface was wetted with H_2O (ℓ), dried by evacuation and treated with $GaMe_3$. The $GaMe_3$ (0.13 mmol) was consumed (15 min at 324°C) producing 0.19 mmol of CH_4. Reaction 5 then took place over the resulting surface.

The reaction of $MeSiH_3$ with $GaMe_3$ also was examined in a reaction vessel without beads. Methylsilane (0.14 mmol) and $GaMe_3$ (0.18 mmol) were allowed to react at 280°C in a new reaction vessel. After 75 minutes, CH_4 (0.07 mmol) was the only volatile product, while all the $MeSiH_3$ was recovered along with 0.11 mmol of $GaMe_3$.

The result from reaction 1 (Table 2) implies that no gas-phase reaction occurs between SiH_4 and $GaMe_3$ at 324°C. Thus it would appear that reactions 3—5 (Table 2) and the SiH_4 reactions listed in Table 1 were surface-"catalyzed." Since $MeSiH_3$ did not react with $GaMe_3$ at 280°C in the unpacked reaction vessel, it would appear that the $MeSiH_3$ reaction listed in Table 1, in a packed reaction vessel, occurred on the surface. We conclude that the methylation of silicon—hydrogen bonds by $GaMe_3$ in our system was probably surface "catalyzed." In an effort to determine whether the active sites are regenerated during reaction, a series of five reactions between $GaMe_3$ and SiH_4 was carried out repetitively at 320°C in an unpacked reaction vessel in which a reaction occurred similar to that of reaction 2 (Table 2). The methylation yield (determined by the quantity of silicon—carbon bonds formed) decreased with each run with the yield in the fifth reaction only 15% of that from the first reaction. The decrease in yield implies that the active sites were consumed as the reactions occurred. It is interesting to note that reactions 3—5 (Table 2) took place only after some gallium moiety was deposited. This result suggests that gallium has some effect on the active site.

We have examined the surfaces used for the reactions listed in Table 1 in an attempt to gain some insight into the surface reactions. After normal cleaning, the effective surface area was determined to be about 20 sq. meters by the BET method [6] with N_2 adsorption at —196°C. A typical surface also was allowed to react with $GaMe_3$ (0.31 mmol) for 10 sec at 250°C, generating 0.23 mmol of CH_4. This reaction cannot be due to the gas-phase thermolysis [7].

Hydroxyl groups bound to silica react with Al_2Me_6 as described in eq. 1

$$-\overset{|}{\underset{|}{Si}}-OH + AlMe_3 \rightarrow -\overset{|}{\underset{|}{Si}}OAlMe_2 + CH_4 \qquad (1)$$

[8]. These hydroxyl groups remain bound to silica at temperatures up to 700°C [8]. It would appear that $GaMe_3$ reacted with our surfaces as described by eq. 2 *. It has also been reported that surface bound hydroxyl groups react with

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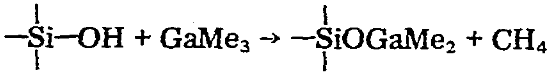
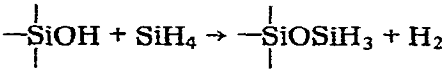
* It is interesting to note that this result, coupled with the 20 sq. meter effective surface area determination, yields a concentration of about 6 hydroxyl groups per 100 Å^2. This concentration is close to that of hydroxyl groups on silica [8].



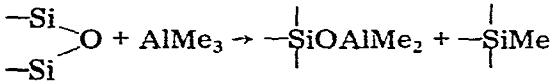
$$-\overset{|}{\underset{|}{Si}}-OH + GaMe_3 \rightarrow -\overset{|}{\underset{|}{Si}}OGaMe_2 + CH_4 \quad (2)$$

SiH_4 at 250°C as described in eq. 3 [9].



$$-\overset{|}{\underset{|}{Si}}OH + SiH_4 \rightarrow -\overset{|}{\underset{|}{Si}}OSiH_3 + H_2 \quad (3)$$

It is tempting to speculate that the silicon—hydrogen methylation reactions occur between a gallium-bound moiety as formed by eq. 2 and a silicon-bound moiety formed by eq. 3. The protons of some hydroxyl groups bound to silicon in SiO_2/Al_2O_3 are very acidic [10]. The presence of gallium next to a silicon-bound hydroxyl group may also enhance the proton acidity, which would facilitate the reaction represented by eq. 3. The rupture of a silicon—oxygen bond via methylation has presumably been observed during the reaction of SiO_2 with Al_2Me_6 [8].



$$\begin{matrix}-Si \\ -Si\end{matrix}\!>\!O + AlMe_3 \rightarrow -\overset{|}{\underset{|}{Si}}OAlMe_2 + -\overset{|}{\underset{|}{Si}}Me$$

The reactions of $GaMe_3$ with Si_2H_6 did not produce methyldisilanes but generated the methylmonosilanes. In a control reactions, $MeSi_2H_5$ (0.06 mmol) was exposed to a typical surface (packed vessel after numerous methylation reactions) for 60 minutes at 265°C after which time all of the $MeSi_2H_5$ was recovered while no volatile products were observed.

The reaction of $GaMe_3$ with PH_3 and AsH_3 also was examined under conditions similar to those listed in Table 1. While the reagents were consumed, the only volatile products were H_2 and CH_4. The solid products from these reactions are of the form $Me_{3-x}GaEH_{3-x}$ where E = P or As [11,12].

A comparison of the results listed in Table 1 show that the H_2 formed/CH_4 formed ratio was greatly increased for the reactions with GeH_4 and B_2H_6. This may be due to gas-phase free radical routes for these methylation reactions. Since C_2H_6 was formed in a few of the silane reactions, CH_3 radicals (formed in the gas phase or on the surface) may also be involved in the silane methylation reactions.

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