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The Preparation and Properties of the Germyltrihydroaluminate Ion

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Abstract

Germane (GeH_4) and $LiAlH_4$ in etheral solvents react, liberating H_2 and forming $LiGeH_3AlH_3$. Reaction of $KGeH_3$ with AlH_3 yields $KGeH_3AlH_3$ along with other less well-defined products. The $GeH_3AlH_3^-$ ion is marginally stable in solution at 25 °C, and decomposes rapidly upon solvent removal. The $GeH_3AlH_3^-$ ion-containing solutions are characterized by IR and ^1H NMR spectral data and analysis of H_2O, HCl and DCl cleavage products. The $GeH_3AlH_3^-$ ion functions poorly as a germylating agent; with CH_3I or Me_3SiBr, low yields of CH_3GeH_3 or Me_3SiGeH_3, respectively arise. The relative importance of $GeH_3AlH_3^-$ ion secondary reactions which involve the $GeH_3AlH_3^-$ ion alone, or it with GeH_4 or the AlH_4^- ion, are discussed.

Introduction

Isolatable compounds which contain germanium–aluminum bonds are rare [1, 2] although such species as intermediates in alkylalane–halogermane [3, 4] and germylarsine–$LiAlH_4$ reactions have been suggested [5]. The known stable compounds $K(Ph_3GeAlH_3)$ [1] and $(Me_3Ge)_3Al$ THF [2], contain complete organo-group substitution at germanium. No examples of germanium hydride derivatives analogous to $K(GeH_3BH_3)$ [6] have been reported. In view of this, our interest in new germyl-group (GeH_3) transfer agents, and the desire to find novel GeAl solid materials precursors, we have studied reactions which occur between GeH_4 and the AlH_4^- ion and between $KGeH_3$ and AlH_3. The results are described below.

Experimental

Apparatus and Materials

Air-sensitive materials were handled in standard vacuum line or N_2-flushed glove bag apparatus [7]. Non-condensible gases were collected and measured using a calibrated Toepler pump. ^1H NMR spectra were obtained at 60.0 and 100.0 MHz with Varian A-60A and HA-100 spectrometers, respectively. Chemical shifts were measured relative to internal Me_4Si; $+\delta$ shifts are downfield from the standard. Infrared spectra were obtained using a Beckman IR-20 spectrometer. Gaseous samples were analyzed in 10 cm cells equipped with KBr windows. Mass spectra (70 eV) were collected with a Varian MAT CH5 spectrometer.

Germane (GeH_4) was prepared and purified by standard techniques [8]. GeH_3D was obtained from $LiAlD_4$ reduction of GeH_3Br; monodeuteration was ascertained from IR and mass spectral data [9]. DCl (>95% D) was prepared from reaction of $SiCl_4$ with D_2O [10]. $LiAlH_4$ (Metal Hydrides, Inc.) was recrystallized from Et_2O. $AlCl_3$ (Matheson, Coleman, and Bell) was sublimed immediately before use. Me_3SiBr (K and K Laboratories) and CH_3I (Matheson, Coleman, and Bell) were distilled. Monoglyme, diglyme, and tetrahydrofuran were triply-distilled from $LiAlH_4$ and stored under N_2.

Synthesis of $LiGeH_3AlH_3$ Solutions

(a) GeH_4 with $LiAlH_4$

Germane at *ca.* 2 atm pressure was allowed to react with $LiAlH_4$ in ether solvents at temperatures between ambient (25–27 °C) and 95 °C in a 500 ml bulb typically under conditions shown in Table I. After reaction, H_2 and excess GeH_4 were removed and measured. Although ambient temperature reactions were extremely slow, requiring months to approach 1:1 GeH_4:AlH_4^- reaction ratios, these solutions remained clear and colorless. Optimum reaction temperature was determined to be 95 °C. Reactions at 95 °C were allowed to proceed until solution discoloration began, the time in which a 1:1 GeH_4–AlH_4^- reactant ratio is approached. Further heating causes deeper discoloration and evolution of additional H_2.

Attempts to obtain crystalline salt products by controlled removal of solvent at 0 °C or by salting out with CH_2Cl_2 or C_6H_6 resulted instead in immediate evolution of H_2, GeH_4 [11], traces of Ge_2H_6 [12], and formation of intractable orange solid.

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TABLE I. Reactions of GeH_4 with $LiAlH_4$

Experiment	Temperature (°C) Solvent[a] Time[b]	Reactants (mmol)		H_2 evolved	GeH_4 : $LiAlH_4$ (reacted)	Cleavage products[c,d]
		$LiAlH_4$	GeH_4			
1	24–27 digl 195 d	5.83	3.40	3.43	0.58	nm[e]
2	24–27 digl 165 d	2.80	2.46	2.69	0.88	GeH_4[f] (2.30) H_2 (7.84) Ge_2H_6 (0.02)
3	95 digl 3 h	5.98	6.20	nm	1.04	GeH_4 (2.68)[g] GeH_3Cl (1.38) H_2 (18.4) Ge_2H_6 (0.05) Ge_3H_8 (<0.01)
4	95 digl 4.5 h	5.15	5.35	6.11	1.04	GeH_4 (4.22) H_2 (13.7) Ge_2H_6 (0.26)
5	95 monogl 5 h	6.01	4.55	5.12	0.76	nm
6	95	5.21	5.21	5.83	1.00	nm
7	95 THF 5.8 h	3.70	4.77	5.00	1.30	nm

[a] Abbreviations: digl, diglyme; monogl, monoglyme; THF, tetrahydrofuran. [b] Abbreviations: d, day; h, hours; min, minutes. [c] Millimole quantities in parentheses. [d] Cleavage with H_2O, unless otherwise specified. [e] Quantity not measured. [f] Products characterized by IR spectra: GeH_4, ref. 11; Ge_2H_6, ref. 12; GeH_3Cl, ref. 14; Ge_3H_6, ref. 12. [g] Cleavage with HCl.

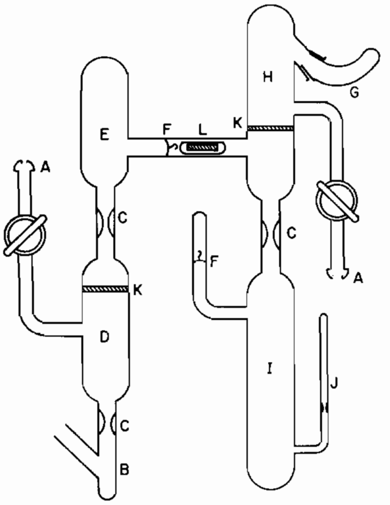

Fig. 1. $KGeH_3$–AlH_3 reaction apparatus: A, vacuum line attachment sites; B, potassium introduction vessel; C, seal-off constrictions; D, potassium + GeH_4 reaction chamber; E, $KGeH_3$ storage vessel; F, break seal; G, $AlCl_3$ introduction tube; H, AlH_3 formation vessel; I, $KGeH_3$ + AlH_3 reaction vessel; J, NMR tube; K, medium porosity fritted filters; L, magnetic breaker.

(b) $KGeH_3$ with AlH_3

Reactions of $KGeH_3$ with AlH_3 in diglyme were carried out in the apparatus shown in Fig. 1. $KGeH_3$ [6] (0.80 mmol) was prepared at D from potassium (sublimed into D from B) and excess GeH_4 in diglyme (3 ml). The $KGeH_3$ was filtered through the frit into receiver E and maintained at –196 °C until needed for reaction with the AlH_3 solution. The AlH_3 [13] was prepared in the inverted apparatus at H. $AlCl_3$ (0.38 mmol) from G was added to $LiAlH_4$ (0.80 mmol) in diglyme at 25 °C in H. After reaction, the apparatus was inverted to allow filtration of the reaction solution into I. The $KGeH_3$ solution was then added from E to the AlH_3 solution in I at –196 °C and the mixture was warmed to –63 °C for 10 h during which time reaction occurred. Traces of H_2 formed. Samples for NMR spectra were removed directly in NMR tubes at J.

Characterization Studies

(a) Hydrolyses

Excess H_2O was condensed at –196 °C into the GeH_4–$LiAlH_4$ or $KGeH_3$–AlH_3 reaction solution. The mixtures were warmed to 25 °C for 15 min, after which time H_2 and volatile hydrolysis products were removed *in vacuo*. These were separated by low-temperature fractional distillation and characterized. No attempt was made to analyze non-volatile residues. Data for $LiGeH_3AlH_3$ from GeH_4–$LiAlH_4$ reactions (experiments 2 and 4) are shown in Table I.

A $KGeH_3$–AlH_3 reaction solution (from 2.20 mmol $KGeH_3$ and 2.20 mmol AlH_3) when allowed to react with excess H_2O yielded H_2, GeH_4 [11] (1.40 mmol), Ge_2H_6 [12] (0.12 mmol) and traces of higher germanes.

$LiGeH_3AlH_3$ solutions from GeH_4–$LiAlH_4$ (prepared as in experiment 4) and $KGeH_3$–AlH_3 reactions were allowed to react briefly, typically 5–10 min at 25 °C, with 1.2 M DCl in D_2O. The monogermane which formed was removed, purified by passage through a −196 °C trap, and subjected to mass spectral analysis (Table II).

TABLE II. Mass Spectral Analysis of Monogermanes[a,b]

m/e	Control samples		Deuterolysis products	
	GeH_4	GeH_3D	$LiAlH_4$–GeH_4	$KGeH_3$–AlH_3
70	17.8	14.1	17.4	16.2
71	11.2	5.7	6.7	6.8
72	69.4	44.1	47.9	46.5
73	64.1	44.7	45.8	46.5
74	94.1	90.0	91.6	92.9
75	91.2	62.4	61.2	64.3
76	100.0	100.0	100.0	100.0
77	78.2	70.7	68.8	72.0
78	16.1	67.1	66.6	66.0
79	15.4	11.8	16.1	13.6
80	<0.5	12.1	15.7	11.9
81	–	<0.5	1.1	<0.6
82	–	–	1.2	0.4

[a] Polyisotopic spectral data; values based on the average of three analyses. [b] Percent intensities relative to the base peak at *m/e* 76.

(b) Anhydrous HCl cleavage

$LiGeH_3AlH_3$ in diglyme was allowed to react with excess HCl (experiment 3). After 45 min, volatile reaction materials were removed *in vacuo*, separated and characterized.

(c) Spectral data: IR

Infrared spectra of GeH_4–$LiAlH_4$ and $KGeH_3$–AlH_3 reaction solutions were obtained on samples under N_2 pressed between CsCl plates. Spectra of samples from GeH_4–$LiAlH_4$ reactions show absorptions at (diglyme absorptions subtracted from spectrum) 1940(s), 1700(s), 765(s), 710(s), 665(w), 605(m), 405(vw), and 365(vw) cm^{-1}. Samples of $KGeH_3$–AlH_3 reaction solutions were closely similar, but with additional weak absorptions at 1955 and 680 cm^{-1}.

(d) ^1H NMR

Diglyme solutions of $LiGeH_3AlH_3$, from GeH_4–$LiAlH_4$ reactions, exhibit a broad singlet at δ 1.87 ppm (GeH_3 protons). Broad resonance lines due to protons on Al could not be unambiguously assigned. The $KGeH_3$–AlH_3 reaction solutions yielded a resonance at δ 1.87 ppm and a lesser resonance of varying intensity at δ 2.02 ppm.

(e) Reactions with Me_3SiBr or CH_3I

A diglyme solution of a GeH_4–$LiAlH_4$ reaction mixture prepared from 5.21 mmol GeH_4 and 5.21 mmol $LiAlH_4$ (experiment 6 reaction mixture) was allowed to react with 22.9 mmol of Me_3SiBr for 10 min at 0 °C. During this time the reaction mixture turned light-orange. Volatile reaction materials consisted of GeH_4 [11] (1.37 mmol), Me_3SiH [15] (13.4 mmol); Me_3SiGeH_3 [16] (0.09 mmol), Ge_2H_6 [12] (0.05 mmol), and unreacted Me_3SiBr (9.15 mmol).

Diglyme solutions of GeH_4–$LiAlH_4$ reaction mixtures prepared at 95 °C were allowed to react with excess CH_3I: (i) a reaction solution from 10.8 mmol $LiAlH_4$ and 9.8 mmol GeH_4, when allowed to react with 16.4 mmol of CH_3I for 10 min at 25 °C, yielded a H_2–CH_4 mixture (6.14 mmol) along with GeH_4 [11] (0.43 mmol), CH_3GeH_3 [17] (0.17 mmol), and Ge_2H_6 [12] (1.1 mmol); (ii) a solution from 3.70 mmol GeH_4 and 2.77 mmol of $LiAlH_4$, when allowed to react with CH_3I for 60 min at 25 °C, yielded a H_2–CH_4 mixture (4.64 mmol), GeH_4 [11] (0.42 mmol), CH_3GeH_3 [17] (0.06 mmol), Ge_2H_6 [12] (0.90 mmol), $CH_3Ge_2H_5$ [18] (0.20 mmol), and traces of $CH_3(GeH_2)_nGeH_3$ [18].

Results and Discussion

Lithium tetrahydroaluminate reactions with excess GeH_4 in glyme ethers or tetrahydrofuran were studied at temperatures between 25 °C and 95 °C under conditions given in Table I. Reaction progress was monitored by periodically measuring the evolved H_2 [H_2(evol.)]. Reactions were taken as complete when H_2 evolution slowed or essentially stopped. At completion of reaction the GeH_4 consumed [GeH_4(react.)] was determined and the resulting reaction solutions were analyzed. At all temperatures studied, reaction proceeded smoothly to the eventual uptake of one equivalent of GeH_4, consistent with the reaction

$$GeH_4 + LiAlH_4 \longrightarrow H_2 + LiGeH_3AlH_3 \qquad (1)$$

At 25 °C, reaction is slow and requires months to reach a GeH_4(react.)/$LiAlH_4$(react.) ratio of one. Reaction proceeds faster at higher temperatures, typically approaching a unit GeH_4(react.)/$LiAlH_4$(react.) ratio in several hours. Initially, at 25 °C, the GeH_4(react.)/H_2(evol.) ratio is close to unity (experiment 1); however, as reaction approaches one equivalent of GeH_4 consumed, the ratio decreases, typically to *ca.* 0.85–0.90 (e.g. experiment 2). The GeH_4(react.)/H_2(evol.) ratio in 95 °C reactions is <1 from the outset (experiment 4) and these reactions are accompanied by distinct solution discoloration near reaction end, suggesting the involvement of Ge–Ge bond forming secondary reactions.

Reaction of $KGeH_3$ with AlH_3, analogous to that of $KGeH_3$ with B_2H_6 used to form $KGeH_3BH_3$ [6], was examined as a possible alternative route to solutions of the $GeH_3AlH_3^-$ ion, according to

$$KGeH_3 + AlH_3 \longrightarrow KGeH_3AlH_3 \qquad (2)$$

Reactions were carried out in the apparatus shown in Fig. 1. This method is very tedious because both $KGeH_3$ [6, 18, 19] and AlH_3 [13, 20] are thermally unstable and must be handled with care during the reaction. Upon mixing the $KGeH_3$ and AlH_3 solutions at –63 °C, slight discoloration of the reaction solution and the evolution of traces of H_2 occurred.

Characterization of the GeH_4–$LiAlH_4$ and $KGeH_3$–AlH_3 reaction solutions has been accomplished by a combination of spectral (IR and ^1H NMR) and solution protolysis (H_2O, D_2O, and HCl cleavage) data. Infrared spectra of the GeH_4–$LiAlH_4$ and $KGeH_3$–AlH_3 reaction solutions are closely similar; however, the spectrum of the $KGeH_3$ reaction solutions contain several weak and unassigned extra absorptions. The GeH_4–$LiAlH_4$ solutions exhibit absorptions at 1940 and 1700 cm^{-1} attributable to Ge–H and Al–H absorptions, respectively. The Ge–H absorption is at lower frequency than most other germanes [11–13, 17] but is comparable to that seen in $KGeH_3BH_3$ (1930 cm^{-1}) [6]. The Al–H absorption in $LiAlH_4$ [21] occurs at 1740 cm^{-1}. The weak absorption at 365 cm^{-1} is tentatively assigned to the Al–Ge bond stretch, although this absorption in other Ge–Al bond-containing compounds [1, 2] has not been reported.

^1H NMR spectra show a singlet resonance at δ 1.87 ppm, attributable to the GeH_3 moiety, and close to that (δ 2.30 ppm) reported for the GeH_3 protons of $KGeH_3BH_3$ [6]. Spectra above 25 °C were not obtained because of the solution's thermal instability. Resonances clearly attributable to Al–H protons were not seen, apparently a situation similar to that found for the $Ph_3GeAlH_3^-$ ion [1]. This most likely results because of ^{27}Al quadrapolar relaxation effects.

Deuterolysis of GeH_4–$LiAlH_4$ and $KGeH_3$–AlH_3 reaction solutions by their reaction with DCl/D_2O yields germane whose isotopic composition can be compared with that of pure GeH_4 [11] and GeH_3D [9] (Table II). From both sources, the germane obtained is primarily GeH_3D, although small amounts (<10%) of more highly deuterated material (e.g. GeH_2D_2 and $GeHD_3$) are present. The germane from the $KGeH_3$–AlH_3 system contains less $GeHD_3$ than that from the GeH_4–$LiAlH_4$ reaction. From both reactions the major reactive species is clearly the GeH_3 unit. Thus, large quantities of germanium moieties which are bonded to more than one hydridoaluminate species simultaneously ($\geqslant$GeH or $\rangle$$GeH_2$) are not present.

Additional characterization of solution reaction species and inferences about the nature of secondary reactions are based on analyses of the protolysis (H_2O or HCl cleavage) reactions. Hydrolysis of 25 °C GeH_4–$LiAlH_4$ solutions yielded GeH_4 [GeH_4(prot)] and H_2 [H_2(prot)] in agreement with eqn. (3), consistent with the presence of the GeH_3-AlH_3^- ion.

$$LiGeH_3AlH_3 + 4H_2O \longrightarrow GeH_4 + LiAl(OH)_4 + 3H_2 \qquad (3)$$

Hydrolysis of 95 °C solutions (e.g. experiment 4) yielded H_2, GeH_4, and small quantities of higher germanes, mainly Ge_2H_6. In all cases, the GeH_4(react.)/GeH_4(prot.) ratio was greater than unity (>1) and the H_2(prot.)/GeH_4(prot.) ratio exceeds 3 (>3). The total recovered Ge (sum of recovered GeH_4, Ge_2H_6, and higher germanes) amounted to 85–95% of the total Ge [based on GeH_4(react.)] in the system. Reactions with HCl were more complex, yielding both GeH_4 and GeH_3Cl and small amounts of Ge_2H_6 and Ge_3H_8. Generally in these, only 65–80% of the total Ge was recovered.

Four secondary reactions (eqns. (4)–(7)) which might be considered in the GeH_4 reaction and which could account for the observed reaction stoichiometry and protolysis products are

$$GeH_4 + GeH_3AlH_3^- \longrightarrow (GeH_3)_2AlH_2^- + H_2 \qquad (4)$$

$$GeH_4 + GeH_3AlH_3^- \longrightarrow Ge_2H_5AlH_3^- + H_2 \qquad (5)$$

$$GeH_3AlH_3^- + AlH_4^- \longrightarrow AlH_3GeH_2AlH_3^{2-} + H_2 \qquad (6)$$

$$2GeH_3AlH_3^- \longrightarrow AlH_4^- + Ge_2H_5AlH_3^- \qquad (7)$$

An analysis of the qualitative effect each of these reactions would have on the theoretical GeH_4(react.)/$LiAlH_4$(react.), GeH_4(react.)/H_2(evol.), GeH_4(react.)/GeH_4(prot.), and H_2(prot.)/GeH_4(prot.) ratios, and the experimentally observed ratios are summarized in Table III. The observed GeH_4(react.)/H_2(evol.) ratio is <1. Thus reaction of additional GeH_4 with $GeH_3AlH_3^-$ (eqn. (4)) to form more highly germylated species such as $(GeH_3)_2AlH_2^-$ as occurs in PH_3–$LiAlH_4$ [22, 23] and AsH_3–$LiAlH_4$ [24] reactions, is not a major process.

The observed GeH_4(react.)/H_2(evol.) and GeH_4(react.)/GeH_4(prot.) ratios are always slightly less than (<1) and greater than unity (>1), respectively. Participation of reactions (5)–(7) seems likely. Reac-

TABLE III. Analysis of GeH_4–$LiAlH_4$ Reaction Reactant and Hydrolysis Product Ratios

Equation	Initial reaction		Hydrolysis reaction	
	$\frac{GeH_4\text{ (reacted)}}{LiAlH_4\text{ (reacted)}}$	$\frac{GeH_4\text{ (reacted)}}{H_2\text{ (evolved)}}$	$\frac{GeH_4\text{ (reacted)}}{GeH_4\text{ (protolized)}}$	$\frac{H_2\text{(protolized)}}{GeH_4\text{ (protolized)}}$
Calculated ratios				
1	1	1	1	3
4	>1	>1	1	<3
5	>1	1	>1	3
6	<1	<1	1	>3
7	>1	1	>1	>3
Observed ratios				
	ca. 1	<1	>1	>3

tion (6) could account for excess H_2 obtained in protolysis reactions and for the GeH_2D_2 among the GeH_4–$LiAlH_4$ reaction product deuterolysis products. Reaction (5) and (7) could be the source of species which yield the higher germanes found among the H_2O and HCl protolysis products. Reaction (5) might be expected since Ge_2H_6 and other GeH_3-substituted compounds (e.g. $GeH_3C_5H_5$ [25]) are known to undergo reaction to more highly catenated products under thermolysis conditions. Decomposition of the $GeH_3BH_3^-$ ion, in a process analogous to that in eqn. (7), has been reported previously [6].

It is interesting to note the difference in thermal stability between the $GeH_3AlH_3^-$ and $GeH_3BH_3^-$ ions. The latter, as the potassium salt can be crystallized from glyme ethers [6]. The compound melts at 98–99 °C with little decomposition. In contrast, $LiGeH_3AlH_3$ or $KGeH_3AlH_3$ when freed of solvent *in vacuo* or when 'salted out' by addition of a second solvent, evolves H_2, GeH_4, and Ge_2H_6 and undergoes immediate color change from colorless to deep orange.

Reactions of $LiGeH_3AlH_3$ with CH_3I and Me_3SiBr indicate that $LiGeH_3AlH_3$ has only limited value as a germylating agent. Reaction with CH_3I yielded 4–5% CH_3GeH_3, along with larger amounts of GeH_4, $CH_3Ge_2H_5$, Ge_2H_6 and CH_4. Similarly, $LiGeH_3AlH_3$ with excess Me_3SiBr produces 1–2% yields of Me_3SiGeH_3 along with Me_3SiH, GeH_4, and Ge_2H_6. Methane and Me_3SiH likely arise from hydroaluminate species reduction of CH_3I and Me_3SiBr, respectively. Germane and Ge_2H_6 formation indicates participation of other more complex processes, perhaps involving the germylene $[GeH_2]$ intermediate as has been suggested to be the case for $KGeH_3BH_3$ [6].

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