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April 1967

Contribution from the Department of Chemistry of the
University of California and the Inorganic Materials Research Division
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Reactions of Silane, Germane and Stannane with Metal- and Amide-Ammonia Solutions

By Douglas S. Rustad and William L. Jolly

Abstract

Germane reacts with liquid ammonia solutions of potassium or potassium amide at -77° to form potassium germyl, germanium imide, and hydrogen gas. The fraction of the germane converted to germanium imide increases with increasing potassium concentration, but remains constant with increasing potassium amide concentration. Amide ion is an intermediate in the reaction of germane with metal-ammonia solutions. In the case of silane, the main reaction is ammonolysis, whereas in the case of stannane, no ammonolysis occurs. A general mechanism is proposed to explain the results.

Introduction

It has been reported by Kraus and his coworkers[1,2] that sodium germyl ($NaGeH_3$) and potassium germyl ($KGeH_3$) can be prepared quantitatively by passing germane through liquid ammonia solutions of the appropriate metals.

$$e^- + GeH_4 \rightarrow GeH_3^- + 1/2\ H_2 \qquad (1)$$

However, when Emeléus and Mackay[3] conductimetrically titrated sodium-ammonia solutions with germane, hydrogen gas in excess of that required by equation 1 was evolved. Early attempts in this laboratory to prepare pure potassium germyl also failed, as evidenced by excess hydrogen gas evolution.[4] Because of these conflicting results, we have reinvestigated the reaction of germane with metal-ammonia solutions. Less extensive studies of silane and stannane have also been carried out. From the results of these studies, we propose a mechanism for the reactions.

Experimental Section[5]

General. - Standard vacuum line techniques were employed in handling volatile materials. Ammonia was purified with potassium. Silane[6] and germane[7] were prepared and purified by standard methods. Stannane was generously supplied by Mr. John Webster. The identity and purity of volatile materials were determined by infrared spectrometry, mass spectrometry, molecular weight determinations, and vapor pressure measurements.

Germanium was determined volumetrically[8] and chloride was determined gravimetrically.

Typical Procedures. - A typical reaction vessel was constructed from a 2.5 x 14 cm Pyrex tube, sealed at one end, with two stopcocks attached in series at the other end. A sealed side-arm was attached between the stopcocks and a glass still for the introduction of sodium or potassium was connected to the main tube via a constriction. The metal-ammonia solutions were prepared by successive distillations of metal and ammonia into the reaction vessel; for some experiments amide was formed (in amounts measured by the evolved hydrogen) by use of a withdrawable rusty-nail catalyst.

Results

Reactions of Germane with the Electron. - The results of experiments in which excess germane was allowed to react with metal-ammonia solutions are presented in Table I. Note that runs 1-7 differed from runs 8-10 in the manner of introducing the germane to the metal-ammonia solutions (see Table I). For each set of runs, the excess hydrogen gas (expressed as a percentage of that expected from reaction 1) increased with increasing metal concentration. At very low electron concentrations potassium germyl was obtained almost quantitatively. These results are consistent with the findings of Teal and Kraus[2] (who obtained nearly quantitative results at very low metal concentrations) and of Emeléus and Mackay[3] (who obtained about 6% excess hydrogen at approximately 0.2 molar metal).

Table I

Reactions of Germane with Potassium-Ammonia Solutions at -77°

	1	2	3	4	5	6	7	8
Run	e^- conc., Molal.	GeH_4 reacted, mmoles	H_2 evolved, mmoles	% excess H_2	$Ge(NH)_2$ calcd, mmoles	GeH_3^- calcd, mmoles	GeH_4, H_2O rx., mmoles	CH_3GeH_3, CH_3Cl rx., mmoles
1[a]	2.38	6.18	4.30	39.2	0.346	5.83		5.90
2[a,b]	2.02	5.15	3.28	27.2	0.200	4.95		4.94
3[a,b]	1.55	4.28	2.51	17.3	0.108	4.17	4.11	
4[a]	0.99	3.28	1.84	12.2	0.057	3.22		
5[a]	0.39	2.40	1.27	5.80	0.020	2.38		2.35
6[a]	0.11	1.12	0.586	4.80	0.008	1.11		
7[a]	0.00842	0.272	0.138	1.47				
8[c]	1.93	3.62	2.88	59.1	0.310	3.31	3.32	
9[c]	1.19	1.44	0.986	37.0	0.076	1.36		
10[c]	0.44	1.22	0.769	25.8	0.045	1.18	1.15	
11[c,b]	0.32	1.07	0.711	32.4	0.050	1.02	0.995	
12[c,d]	1.08	2.10	1.28	21.9	0.066	2.03	2.03	

[a] Germane and the metal-NH_3 solution were warmed together from -196° to -77°.

[b] Reaction vessel not shaken.

[c] Gaseous GeH_4 introduced to the liquid metal-NH_3 solution at -77°.

[d] Na was used. In the others, K was used.

In all of the runs (except runs 6 and 7), and especially in the runs with high metal concentrations, a white precipitate formed. On the basis of evidence which we describe below, we believe that this precipitate was germanium imide, $Ge(NH)_2$, (or possibly germanium tetraamide, $Ge(NH_2)_4$) and that the following side reaction gave this product and the excess hydrogen gas:

$$GeH_4 + 2NH_3 \rightarrow Ge(NH)_2 + 4H_2 \qquad (2)$$

Evidence for $Ge(NH_2)_2$ or $Ge(NH_2)_4$. - By assuming that reactions 1 and 2 were the only net reactions taking place between germane and the potassium-ammonia solutions, the amounts of potassium germyl formed were calculated (from the data of columns 2 and 3, Table I) and tabulated in column 6, Table I. In some runs, the potassium germyl was treated with water and thereby quantitatively hydrolyzed to germane (amounts given in column 7). In other runs, the potassium germyl was treated with excess methyl chloride and thereby quantitatively converted to methyl-germane (amounts given in column 8). Where it is possible to compare the data in column 6 with data in column 7 and 8, the agreement is good. Thus the analyses confirm that the side reaction in the reaction of germane with a potassium-ammonia solution involves the evolution of four moles of hydrogen per mole of germane consumed.

In runs 1 and 2, the white solid which remained after removing all the methyl chloride and other volatile materials was analyzed for nitrogen and, in run 1, germanium.

Anal. Run 1: Calcd. for $Ge(NH)_2$ (from Table I), N, 0.692 mmole; Ge, 0.346 mmole. Found, N, 0.662 mmole; Ge, 0.335 mmole.
Run 2: Calcd. for $Ge(NH)_2$ (from Table I), N, 0.400 mmole. Found, N, 0.396 mmole.

Germanium tetraamide apparently has never been isolated. Thomas and Pugh[9] attempted to isolate it as -20°, but obtained only the imide, $Ge(NH)_2$. Because our reaction mixtures were ultimately warmed to room temperature, we would not expect to have obtained the amide, even if it had formed at the lower temperature. We shall hereafter arbitrarily refer to the precipitate as the imide, with the understanding that it initially may have been the amide.

Titrations of Potassium-Ammonia Solutions with Germane. - Gaseous germane was added in small increments to a 0.63 molar potassium-ammonia solution at -77°, and after each addition the evolved hydrogen gas was measured. The blue color of the ammoniated electron disappeared at a Σ GeH_4/initial e^- ratio of ca. 0.6. At this point the color of the solution was light yellowish-green, which upon further addition of germane faded. The amount of white precipitate increased with each addition after the electron end point. (The solution was too opaque to see any precipitate before this end point.) The reaction was complete at a GeH_4/initial e^- ratio of ca. 1.13, with 102% excess hydrogen evolution. Clearly the extent of ammonolysis increased upon going from the procedures of the runs in Table I to the titration procedure.

Isolation of Sodium Amide from the Germane-Sodium-Ammonia Reaction. - A sodium-ammonia solution at -77° was treated with a little less than half the equivalent amount of germane. The solution was decanted from the white precipitate, and the latter was washed with distilled liquid ammonia and dried by evacuation. The x-ray powder pattern (obtained by Mrs. Helena Ruben) corresponded closely to that of an authentic sample of sodium amide.

Reactions of Germane with Amide Solutions. - When potassium amide-ammonia solutions were allowed to react with excess germane at -77°, hydrogen was evolved, suggesting that some of the germane ammonolyzed according to reaction 2. The remainder of the germane reacted in the expected way to yield potassium germyl (reaction 3), as evidenced by

$$GeH_4 + NH_2^- \rightarrow GeH_3^- + NH_3 \qquad (3)$$

the fact that germane was formed upon subsequent treatment of the products with water. The quantitative data in Table II support this interpretation. As required by the stoichiometry, the initial amount of amide (column 2) was essentially equal to both the amount of germane evolved upon hydrolysis (column 7) and the amount of potassium germyl (column 5) calculated from the data of columns 3 and 4. It is significant that the same ratio of germanium imide to potassium germyl was formed at two very different amide concentrations.

Table II

Reactions of Gaseous Germane and Potassium Amide-Ammonia Solutions at -77°

	1	2	3	4	5	6	7	8
Run	NH_2^- conc., molal	NH_2^-, mmole	GeH_4 reacted, mmole	H_2 evolved, mmole	GeH_3^- calcd, mmole	$Ge(NH)_2$ calcd, mmole	GeH_4 H_2O rx., mmole	$\frac{Ge(NH)_2}{GeH_3^-}$
1	0.526	2.00	2.31	1.41	1.96	0.352	1.96	0.180
2	0.194	0.896	1.03	0.631	0.872	0.158	0.868	0.181
3	<0.0055	<0.005	<0.005	trace				

Reactions of Silane. - Silane reacted completely with a dilute potassium amide solution to give 4.00 moles of hydrogen gas per mole of silane. After evaporation of the ammonia, hydrolysis of the residue gave 102% of the ammonia expected for $Si(NH)_2$.[10-12] Clearly the silane underwent essentially complete ammonolysis by a reaction analogous to reaction 2.

The reaction of silane with a potassium-ammonia solution was observed to involve principally ammonolysis, with only a small fraction of the silane being converted to potassium silyl. This result is similar to that of Isenberg.[11]

Reaction of Stannane with an Amide Solution. - A potassium amide-ammonia solution was treated with excess stannane at -77°. The potassium amide was converted to the corresponding amount of potassium stannyl, and most of the excess stannane decomposed to the elements. The potassium stannyl was decomposed to hydrogen and KSn, and then the latter was hydrolyzed to KOH, Sn and hydrogen. The ratio of the total hydrogen formed (including the latter batches) to the stannane consumed was 2.015 (theoretical: 2.00); this result indicates that essentially no ammonolysis to tin imide occurred.

Discussion

In their conductimetric titration of sodium-ammonia solutions with germane, Emeléus and Mackay[3] found a minimum, at which point they observed a yellowish-green precipitate assumed to be sodium germylene (Na_2GeH_2).

Our results show that the precipitate was probably sodium amide, colored by amide ions in the liquid ammonia. Potassium amide is sufficiently soluble in liquid ammonia that it does not precipitate during the reaction of germane with potassium-ammonia solutions.

In order to account for the formation of amide ion and germanium imide in the reaction of germane with metal-ammonia solutions, we propose the following mechanism.[13]

$$e^- + GeH_4 \rightarrow GeH_3^- + H \quad (4)$$

$$H + e^- \rightarrow H^- \quad (5)$$

$$H^- + NH_3 \rightarrow NH_2^- + H_2 \quad (6)$$

$$2H \rightarrow H_2 \quad (7)$$

$$GeH_4 + NH_2^- \rightarrow GeH_3^- + NH_3 \quad (3)$$

$$GeH_4 + NH_2^- \rightarrow GeH_3NH_2 + H^- \quad (8)$$

The formation of hydride ion as an intermediate seems plausible because when potassium silyl ($KSiH_3$) is prepared from the reaction of silane with potassium in 1,2-dimethoxyethane, potassium hydride is formed as a by-product.[13,14] We assume that subsequent ammonolysis of GeH_3NH_2 to $Ge(NH_2)_4$ or $Ge(NH)_2$ proceeds rapidly.[16] In this mechanism,[5] one would expect the rate of formation of amide ion (which catalyzes the $Ge(NH)_2$-producing reaction), relative to the rate of reaction 4, to increase with increasing metal concentration. The mechanism thus explains the excess hydrogen formed at high metal concentrations. The same

mechanism is applicable to the analogous reactions of silane and stannane if we assume that, on going from SiH_4 to GeH_4 to SnH_4, the protonic acidity increases and the susceptibility to displacement of hydride ion by amide ion decreases.

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(13) The following reaction[14] is another conceivable source of hydride ion: $GeH_4 + 2e^- \rightarrow GeH_3^- + H^-$. However, we omit this reaction because its inclusion would not change the qualitative conclusions, and because a dinegative activated complex seems implausible to us. In either case, reaction 5 (or a combination of reactions 5 and 6) should be included because the corresponding aqueous reaction proceeds at a diffusion-controlled rate.[15]

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