sign of solid formation. In all cases the starting materials were recovered quantitatively.

More positive results were obtained when the experiments were repeated in small-volume reaction vessels. Typically, monosilylphosphine (0.33 mmole) and diborane (0.16 mmole) were condensed at −196° into a micro nmr tube which was then sealed. When the contents were warmed, a liquid formed which was reasonably stable up to room temperature. Over a period of about 12 hr at room temperature bubbles of gas were formed as the liquid decomposed to a white solid. The tube was then recooled to −196° and opened onto the vacuum line. The volatile products contained no noncondensable gas and were all sufficiently volatile to pass through a trap at −126°. The infrared spectrum of the material was essentially that of monosilane.[20] At high pressure extra peaks at 1602 and 2617 cm^{-1} could be detected and identified as being due to a small amount of diborane,[21] which is the likely impurity of that volatility. Thus the major product of the reaction was monosilane (approximately 0.3 mmole).

Reaction of Monosilylphosphine and Monobromodiborane. 1:1 Addition.—In a typical reaction, monosilylphosphine (0.82 mmole) and monobromodiborane (0.82 mmole) were condensed together at −196° into the 25-ml reaction vessel, warmed to −78°, and held at that temperature for 1 hr. A white solid was formed and the pressure remained negligible even when the temperature was raised to −63°. At −45° volatile products were formed which were separated into two components. The fraction passing through a trap at −126° was diborane (0.40 mmole; mol wt: found, 27.5; calcd, 27.6; identified by its infrared spectrum[21]) and the fraction trapped at −126° was monobromosilane (0.26 mmole; mol wt: found, 110.6; calcd, 111.02; identified by its infrared spectrum[22]). There was much frothing and bubbling when the temperature was raised to −23°. The white solid changed to a viscous transparent liquid and more monobromosilane (0.53 mmole) was evolved. The liquid showed no signs of further decomposition even when it was warmed up to 100°.

Reaction of Monosilylphosphine and Monobromodiborane. 2:1 Addition.—A white solid was formed when monosilylphosphine (0.75 mmole) and monobromodiborane (0.38 mmole) were condensed together under the same conditions as those described for the 1:1 additions and held for 1 hr at −78°. There was no evidence for the formation of diborane when the temperature was raised to −45° although there was a slight increase in the pressure because a small amount of monobromosilane (0.06 mmole) was liberated. On warming to −23°, the solid decomposed with much frothing and bubbling to evolve a mixture of diborane, monosilane, monosilylphosphine, and monobromosilane. The decomposition was not complete until the temperature had been raised to 25°, but, from other experiments where the volatiles were taken off as the temperature was raised in steps, it was apparent that all of the monobromosilane was evolved at −23°. The volatile fraction passing through a −126° trap was the mixture of diborane and monosilane (a total of 0.31 mmole), and the fraction trapped at −126° but passing through a −96° trap was the mixture of monosilylphosphine and monobromosilane (a total of 0.51 mmole).

Acknowledgments.—We wish to thank the Science Research Council for a research grant to J. S. and the London Chemical Society for a grant for the purchase of chemicals.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE
LAWRENCE RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

Reactions of Silane, Germane, and Stannane with Metal- and Amide-Ammonia Solutions

BY DOUGLAS S. RUSTAD AND WILLIAM L. JOLLY

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Germane reacts with liquid ammonia solutions of potassium or potassium amide at −77° to form potassium germyl, germanium imide ($Ge(NH)_2 \cdot xNH_3$), 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 co-workers[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

$$e^- + GeH_4 \longrightarrow GeH_3^- + {}^1/_2H_2 \qquad (1)$$

However, when Emeléus and Mackay[3] conductometrically titrated sodium–ammonia solutions with germane, hydrogen gas in excess of that required by eq 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.

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[2] G. K. Teal and C. A. Kraus, *ibid.*, **72**, 4706 (1950).

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[4] G. Gilbert and W. L. Jolly, unpublished work and preliminary work in this study.

TABLE I

REACTIONS OF GERMANE WITH POTASSIUM–AMMONIA SOLUTIONS AT −77°

Run no.	1 e^- concn, *m*	2 GeH_4 reacted, mmoles	3 H_2 evolved, mmoles	4 % excess H_2	5 $Ge(NH)_2$ calcd, mmole	6 GeH_3^- calcd, mmoles	7 GeH_4, H_2O reaction, mmoles	8 CH_3GeH_3, CH_3Cl reaction, 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,d]	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–ammonia solution were warmed together from −196 to −77°. [b] Reaction vessel not shaken. [c] Gaseous GeH_4 introduced to the liquid metal–ammonia solution at −77°. [d] Na was used. In the others, K was used.

Experimental Section[5]

General Material.—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,[8–12] mass spectrometry, molecular weight determinations, and vapor pressure measurements.[13–15] Volatile mixtures were separated, when possible, by fractional condensation in appropriate cold traps. Ammonia was usually removed from germane and its derivatives by absorption by granular anhydrous magnesium perchlorate. Methylgermane was removed from methyl chloride by treatment with iodine at room temperature, passing the resulting mixture through a −112° trap to remove methyliodogermanes, and washing the remaining material with aqueous sodium hydroxide to remove hydrogen iodide.

Germanium was determined volumetrically[16] and chloride was determined gravimetrically.

Typical Procedure.—A reaction vessel was constructed from a 2.5 × 14 cm Pyrex tube, sealed at one end, with a stopcock at the other end. A glass still for the introduction of sodium or potassium was connected to the 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 *M* metal).

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(IV) imide, $Ge(NH)_2$ (or, better, $Ge(NH)_2 \cdot xNH_3$), and that a side reaction gave this product and the excess hydrogen gas

$$GeH_4 + (2 + x)NH_3 \longrightarrow Ge(NH)_2 \cdot xNH_3 + 4H_2 \quad (2)$$

Evidence for $Ge(NH)_2 \cdot xNH_3$.—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 methylgermane (amounts given in column 8). Where it is possible to compare the data in column 6 with data in columns 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 4 moles of hydrogen/mole of germane consumed.

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

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(5) Further details may be obtained from the Ph.D. thesis of D. S. Rustad, University of California, 1967, UCRL-17602.

(6) A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 2692 (1947).

(7) W. L. Jolly and J. E. Drake, *Inorg. Syn.*, **7**, 34 (1963).

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(12) J. E. Griffiths, *ibid.*, **38**, 2879 (1963).

(13) Vapor pressures were observed to be within ±2% of the literature values for silane,[6] germane,[7] stannane,[7] methyl chloride,[14] and methylgermane.[15]

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TABLE II

REACTIONS OF GASEOUS GERMANE AND POTASSIUM AMIDE–AMMONIA SOLUTIONS AT −77°

Run no.	1 NH_2^- concn, *m*	2 NH_2^- mmole	3 GeH_4 reacted, mmoles	4 H_2 evolved, mmoles	5 GeH_3^- calcd, mmoles	6 $Ge(NH)_2$ calcd, mmole	7 GeH_4, H_2O reaction, mmoles	8 $Ge(NH)_2/GeH_3^-$
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				

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[17] attempted to isolate it at −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 arbitrarily refer to the initial precipitate as $Ge(NH)_2 \cdot xNH_3$.

Titrations of Potassium–Ammonia Solutions with Germane.—Gaseous germane was added in small increments to a 0.63 *M* 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 $\Sigma[GeH_4]/[\text{initial } e^-]$ ratio of *ca.* 0.6. At this point the solution was light yellowish green, which faded upon further addition of germane. 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 $[GeH_4]/[\text{initial } e^-]$ 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 the fact that

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

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.

Reactions of Silane.—Silane reacted completely with a dilute potassium amide solution to give 4.00 moles of hydrogen gas/mole of silane. After evaporation of the ammonia, hydrolysis of the residue gave 102% of the ammonia expected for $Si(NH)_2$.[18–20] 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.[19]

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 conductometric 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

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metal–ammonia solutions, we propose the mechanism[21–23]

$$e^- + GeH_4 \longrightarrow GeH_3^- + H \qquad (4)$$

$$H + e^- \longrightarrow H^- \qquad (5)$$

$$H^- + NH_3 \longrightarrow NH_2^- + H_2 \qquad (6)$$

$$2H \longrightarrow H_2 \qquad (7)$$

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

$$GeH_4 + NH_2^- \longrightarrow GeH_3NH_2 + H^- \qquad (8)$$

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.[21,22] We assume that subsequent ammonolysis of GeH_3NH_2 to $Ge(NH_2)_4$ or $Ge(NH)_2$ proceeds rapidly.[24,25] 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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(21) The following reaction[22] 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.[23]

(22) M. A. Ring and D. M. Ritter, *J. Am. Chem. Soc.*, **83**, 802 (1961).

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(24) The rate-determining step in the formation of $Ge(NH_2)_4$ is probably reaction 8, because the germanium would become more positive as the number of amino groups increases (inductive effect) and, consequently, more susceptible to nucleophilic attack by amide.[25] From the data in Table II, we calculate $k_8/k_3 = 0.18$.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY, PITTSBURGH, PENNSYLVANIA 15231

The Preparation and Properties of Germyl Methyl Ether and Germylmethyl Methyl Ether[1]

BY G. A. GIBBON, J. T. WANG, AND C. H. VAN DYKE

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The synthesis, characterization, and some properties of GeH_3OCH_3 and $GeH_3CH_2OCH_3$ are described. The donor properties of the compounds have been investigated by an infrared hydrogen-bonding study. Germyl methyl ether acts as a stronger Lewis base than $(CH_3)_2O$, and $GeH_3CH_2OCH_3$ acts as a weaker Lewis base than $CH_3CH_2OCH_3$, with methanol as reference acid. The results are compared with data for the corresponding silicon compounds and discussed in terms of electronegativity and π-bonding considerations.

Interest in the structure and bonding of hydrogen compounds of the lower group IV elements continues to be strong. Most of the work reported thus far has been concerned with the silicon hydrides and their derivatives.[2–4] Much less work has been reported for the corresponding derivatives of germanium. Synthesis and stability problems have greatly hindered the study of these latter hydride derivatives and only recently have many of these difficulties been overcome.

Central to an evaluation of the factors which influence the physical properties and bonding in the germanium hydride derivatives is the availability of compounds on which specific physical measurements can be performed. In a previous paper,[5] the preparation of GeH_3OCH_3 was reported as part of a study of the mercury-sensitized photolysis of carbon, silicon, and germanium hydride systems. Only a small amount of material was isolated by using this technique, but contrary to the prediction of earlier workers,[6] the compound was found to be reasonably stable in the vacuum line. This has prompted us to investigate a more conventional preparation of GeH_3OCH_3 and to determine some of its physical and chemical properties. In addition, the new compound germylmethyl methyl ether, $GeH_3CH_2OCH_3$, has been synthesized and studied. The Lewis base strengths of these compounds relative to their silicon and carbon counterparts have been measured to study the basicity of the oxygen atom in the Ge–O–C linkage and the inductive effect of the GeH_3

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(1) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

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