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THE DISPROPORTIONATION OF DIGERMANE IN LIQUID AMMONIA

Robert M. Dreyfuss and William L. Jolly

May, 1968

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

The Disproportionation of Digermane in Liquid Ammonia

By Robert M. Dreyfuss and William L. Jolly

While attempting to measure the acid dissociation constant of digermane in liquid ammonia, we have observed that digermane decomposes in liquid ammonia solution to give germane and a solid germanium hydride of variable composition. Similar base-catalyzed decompositions of digermane have been observed by Bornhorst and Ring,[1] but these workers did not investigate the nature of the solid hydride formed. In view of Glarum and Kraus's earlier report[2] of the formation of GeH_2 by the reaction of bromobenzene with sodium germyl in ammonia, we decided to determine if the same substance can be prepared by the ammonia-catalyzed disproportionation of digermane.

Experimental Section

Standard greaseless vacuum line techniques were employed. Digermane was prepared according to the method of Jolly and Drake.[3] The identity

and purity of germane and digermane were determined by infrared spectrometry[4,5] with a Perkin Elmer Model 137 Infracord spectrometer, by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer, Model 21-620, and by vapor pressure measurements.[3] Ammonia was dried over sodium before its use.

Reactions were carried out in a vessel equipped with two break-off seals. A measured amount of digermane and approximately 0.5 ml of liquid ammonia were distilled into the vessel at liquid nitrogen temperature. The vessel was then sealed and placed in a bath of appropriate temperature. When a low-temperature bath was used, care was taken to keep the entire vessel below the level of the bath.

After reaction had proceeded, the vessel was attached to the vacuum line, and one of the seals was opened, keeping the vessel in the low temperature bath. The volatile contents were then Toepler-pumped through a liquid nitrogen trap until all volatiles had distilled over. A trace of hydrogen could usually be measured in the buret of the Toepler pump. The vessel was then sealed off again and temporarily set aside. The volatiles were then separated. In runs in which all the digermane had decomposed, it was possible to separate germane and ammonia by means of a -160° trap. However, when digermane was present the ammonia could not be separated by trap-to-trap distillation; it was removed by distilling the ternary mixture very slowly through a trap of anhydrous magnesium perchlorate at 0°. The germane and digermane were then separated by fractional condensation in traps at -112° and -196°; the amount of each was determined by pressure-volume techniques.

The residue in the reaction vessel was then pyrolyzed at 400° for two hours. The hydrogen (identified by mass spectrometry) was then Toepler-pumped through the second break-off seal and a -196° trap to remove any ammonia that might have adhered to the solid. The hydrogen was measured and the germanium mirror was either discarded or dissolved in basic hydrogen peroxide and titrated with a pH-meter according to the method of Tchakirian.[6]

Results

The results are presented in Table I. The adequacy of the quantitative measurements is attested by the fact that the hydrogen in the germane produced and that formed in the pyrolysis of the GeH_x accounts for the hydrogen in the consumed digermane with an average discrepancy of ± 1.2%. And in the four runs where a germanium balance could be calculated, the average discrepancy was ± 3.5%.

In the -63° runs, the solution was initially colorless, but on standing the solution turned yellow and a yellow precipitate formed. In the -45° run, a yellow precipitate formed quickly. In the room-temperature runs, a blood red precipitate formed immediately.

Discussion

The results indicate that, in liquid ammonia solution, digermane disproportionates as follows:

$$Ge_2H_6 \rightarrow GeH_4 + GeH_2$$

Table I.

Quantitative Data for Ge_2H_6 Disproportionations

(All quantities in mmoles)

Temp. °C	Time hr.	A Ge_2H_6 in	B Ge_2H_6 out	C GeH_4 formed	D H_2 from GeH_x pyrolysis	E Ge in GeH_x	Calcd. values of x: 2D/E	Calcd. values of x: 2D / 2(A-B)-C
-63	96	0.668	0.273	0.481	0.253	0.264	1.92	1.64 [a]
-63	96	.553	.323	.260	.149	.180	1.66	1.49 [a]
-63	25	.383	.308	.064	.077	.077	2.00	1.79 [a]
-63	25	.536	.479	.0696	.0695	.069	2.01	3.16 [a]
-45	37	.200	0	.220	.169	-	-	1.88
23 [b]	24	.188	0	.244	.0746	-	-	1.13
23	20	.244	0	.334	.0676	-	-	0.88
23 [c]	14	.218	0	.291	.0789	-	-	1.09
23	13	.247	0	.321	.0800	-	-	0.92
23	0.25	.152	.114	.0417	.0316	-	-	1.86 [a]

[a] These values are relatively inaccurate because they require the difficult determination of the unreacted Ge_2H_6 (B).

[b] Ammonia soln. 1 M in NH_4NO_3

[c] $NH_3:Ge_2H_6$ = 1:1

At temperatures above -63° (and even at that temperature on standing), the GeH_2 decomposes to germane and a yellow or red precipitate of GeH_x ($x<2$). The higher the temperature, the more rapidly the GeH_2 decomposes, the lower the value of x and the darker the color of the precipitated GeH_x. Although Glarum and Kraus[2] reported similar properties for GeH_2 prepared from bromobenzene and sodium germyl, their substance was more stable inasmuch as its solution in ammonia did not become colored on standing for 24 hours, and it could be isolated for a short time as a white solid at -33°.

In the hope that the solution at -63° contained a soluble GeH_2 species, the proton magnetic resonance spectrum of a 0.5 M Ge_2H_6 solution was obtained. The spectrum showed peaks corresponding to germane, digermane and a series of three smaller peaks from 8 to 25 cycles upfield from germane, perhaps corresponding to a lower hydride. As the solution decomposed, the digermane peak decreased in amplitude, the germane peak increased, and the little peaks began to merge and broaden. By the time the digermane peak had disappeared, the little peaks were gone. Attempts to get better resolution by increasing the digermane concentration were unsuccessful, probably because of limited solubility of the lower hydride.

Efforts to effect reaction between GeH_2 and acetylene or diphenylacetylene at -63°, in analogy with the high-temperature reactions of GeI_2,[7] were unsuccessful.

We have observed that no reaction occurs when both the digermane and the ammonia are completely in the gas phase; however, reaction proceeds in the presence of even traces of liquid ammonia. The basic catalyst

is ammonia itself and not the amide ion because the reaction goes without noticeable change in 1 M ammonium nitrate liquid ammonia solution. Apparently, relatively weak bases cause the disproportionation of digermane. In addition to ammonia and those bases shown to be effective by Bornhorst and Ring,[1] aqueous sodium hydroxide causes the disproportionation.[8]

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References

(1) W. R. Bornhorst and M. A. Ring, Inorg. Chem., 7, 1009 (1968).

(2) S. N. Glarum, and C. A. Kraus, J. Am. Chem. Soc., 72, 5398 (1950).

(3) W. L. Jolly and J. E. Drake, Inorg. Syntheses, 7, 34 (1963).

(4) For GeH_4: J. W. Straley, C. H. Tindal, and H. H. Nielsen, Phys. Rev., 62, 161 (1942).

(5) For Ge_2H_6: D. A. Dows and R. M. Hexter, J. Chem. Phys., 24, 1029 (1956).

(6) R. Belcher and C. L. Wilson, New Methods in Analytical Chemistry, Chapman and Hall, London 2nd ed., 1956, p. 232.

(7) M. E. Volpin, et al., Izvest, Akad. Nauk SSSR Ser. Chim., 1963, 2067.

(8) L. M. Dennis, R. B. Corey and R. W. Moore, J. Am. Chem. Soc., 46, 657 (1924), and unreported observations of R. Dreyfuss.

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