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THE PREPARATION OF GERMANE*

T. S. PIPER† and M. KENT WILSON‡
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

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Abstract—Germane is conveniently prepared by reduction of an aqueous acidic solution of germanium oxide with sodium borohydride.

INTRODUCTION

PREVIOUS preparations of germane have used the reaction of magnesium germanide with hydrochloric acid[1] or with ammonium bromide in liquid ammonia.[2] Also, germanium tetrachloride may be reduced with lithium aluminium hydride in ether,[3] but the yield is less than 30%. The preparation of stannane by dropping an aqueous solution of sodium borohydride into a solution of tin(II) chloride in dilute hydrochloric acid[4] led us to attempt to prepare germane by a similar reaction. We have found that germane is quite conveniently prepared in 60–75% yields using this method. The unpurified germane was found to contain about 0·6% by volume of digermane.

In an attempt to prepare monodeuterogermane this reaction was carried out in a solution containing 45% deuterium oxide. By estimation from the intensities of infra-red bands of the products it was found that 20 to 25% of the germane molecules contained a deuterium atom. This is interesting in that it indicates that there exists some mechanism of formation of germane other than hydride transfer to the germanium from the borohydride ion if exchange of hydrogen of borohydride ion with water is excluded (sodium borohydride has been shown not to exchange with deuterium oxide at pH = 12).[5] A better method of preparing pure monodeuterogermane was found in the reduction of sodium germanyl[2] with deuterium chloride in di-*n*-butyl ether. The product of this reaction gave an infra-red spectrum in the sodium chloride region which was identical with that reported for monodeuterogermane prepared from trichlorogermane by reaction with lithium aluminium deuteride.[6]

Attempts to prepare plumbane by action of sodium borohydride on divalent lead under similar conditions have failed to produce appreciable gaseous products nor was absorption in the infra-red observed where the lead-hydrogen stretching frequency would be expected. A hydrogen sulphide test on material in the trap where plumbane would have collected gave a slight but dubious test for lead.

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† Present address: Chemistry Department, University of Illinois, Urbana, Illinois.

‡ Present address: Chemistry Department, Tufts University, Medford, Mass.

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EXPERIMENTAL

The reaction was carried out in a three-hundred millilitre, three-necked flask, equipped with dropping funnel, magnetic stirrer, and a reflux condenser. The condenser led to a manifold with a mercury manometer and thence through two U-traps to a vacuum pump. The first trap was made from 20-mm glass tubing while the second which connected directly to the pump was made from 7-mm tubing.

Germanium oxide (0·2995 g) was dissolved in boiling 1 M hydrobromic acid (150 ml) in the flask. The solution was then cooled with an ice bath. Sodium borohydride (2 g) dissolved in water (40 ml) was placed in the dropping funnel. Both traps were placed in liquid nitrogen. The second trap was evacuated and the stopcock between it and the first trap was set to give a slow leak. When the pressure in the flask, manifold, and first trap was reduced to 10 or 20 cm the sodium borohydride solution was slowly dropped into the flask to maintain this pressure. In all, 6 g of sodium borohydride was added in 2 g portions. After the addition of each portion, the material in the first trap volatile at −78°C was transferred to the second. Of this crude product 58% was collected with the first portion of sodium borohydride and 92% with the first two portions. The crude germane was then purified by distillation through a trap at −100°C to give 550 ml of gas at 71 mm and 27°C or 47·2 ml S.T.P., a yield of 73%. There was no appreciable germanium left in solution: a slight metallic mirror on the inside of the reaction flask indicated the remaining germanium had been reduced to the element.

The germane was found to be quite pure by examination of its infra-red spectrum. In another experiment 700 ml (S.T.P.) of germane were prepared and it was carefully fractionated through a trap held at −140°C. The material in the trap amounted to 0·43 ml (S.T.P.) or 0·6% by volume of the original gas. It was found to be digermane by comparison of its infra-red spectrum with that reported previously.[7]

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